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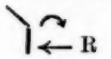
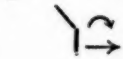
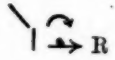
	,, Mechanism, 3 column 2.		
	,, Mechanism 4, column 2.		
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552	15-16	disobeyed	obeyed
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557	39	$C_{26}H_{32}O_2N_2$	$C_{26}H_{36}O_2N_2$
561	4	*p*-Imino-*d*-camphordiphenylamine.	*p*-Imino-*dl*-camphordiphenylamine.
562	31	*p*-amino-*d*-camphordiphenylamine.	*p*-amino-*dl*-camphordiphenylamine.
563	20	H, 7·82 per cent.	H, 7·69 per cent.
571	12	—544·0	—344·0
573	5	—540·7	—530·7
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The Chemical Elements and Compounds *

By Sir P. C. Ray, Kt., C.I.E., DSc., Ph.D.

Our ideas of the nature and properties of the elementary atoms and their compounds have undergone profound changes as the result of the most important investigations in physical science during the last two decades. The old simple Daltonian conception of atoms as the ultimate indivisible particles with constant weights can no longer be accepted without reservations. Every student of physical science now learns that an atom is a very complicated structure resembling the solar system with a positively charged central nucleus —the seat of the entire weight of the atom—surrounded by a number of electrons or negative units of electricity moving rapidly in definite circular and elliptical orbits. This modern Rutherford-Bohr model of atom has invaded our chemical science and a host of eminent workers are busy in illuminating many obscure branches of chemistry, systematising and unifying the entangled mass of uncoordinated facts,—in other words, building cosmos out of chaos—specially in the inorganic branch of chemistry which has suffered so long from the reproach of being simply a collection of dull and insipid facts with no underlying theoretical basis.

The most fundamental problem of chemistry which has engaged the serious attention of the chemists since the enunciation of Daltonian hypothesis, is the combining power or the valency of the atom. The cause of this combining power and its variability has long remained in the dark in spite of numerous hypotheses and speculations on the subject. But since the development of the modern atomic structure, entirely new light has been thrown on it and it is hoped that in no distant future the chemists will be in a position to unravel this fundamental mystery of their science and even to predict the nature and properties of unknown compounds just as they have done with

* Presidential address to the Indian Chemical Society delivered on 5th January, 1930 at Allahabad.

the unknown elements of which the discovery of hafnium furnishes a striking instance. Notable progress has already been made in this direction and several theories of valency—and I must admit that some of them of even conflicting nature—are trying to establish and hold their position in the chemical literature. The most generally accepted view as has been developed by Kossel, Lewis, Langmuir and Sidgwick can briefly be summarised as follows:

The elementary atoms are not all equally stable. Hence they readily combine with other atoms or even with themselves to form what are known as compounds or simple molecules. There are, however, only a few elements represented by the rare gases of the atmosphere whose atoms fail to exhibit any such tendency for combination. Their atoms are regarded as chemically and electrically inert. Hence it is assumed that the atoms of these monatomic gases represent the most stable configurations in the evolution of the elements. All the other elementary atoms, whose structures are comparatively less stable, tend to attain the stable configuration representing their nearest rare-gas neighbour by mutual union. This is regarded as the ultimate cause of chemical combination. The atoms just preceding the rare-gas elements in the natural series of elements can do this by accepting one or more electrons from others and the atoms just succeeding the rare-gases stabilize their configurations by transferring or giving up one or more electrons to their partners in the chemical combination. This exchange, transfer or sharing of electrons are confined to the outermost layer of the atom. These are therefore known as valency electrons.

Two main types of valency are generally recognized These are *polar* or *electro-valency* and *non-polar* or *co-valency*. Polar bonds lead to the formation of ions by transfer of electrons as in the case of NaCl; non-polar or co-valent bonds lead to the formation of non-ionized molecules by sharing of electrons such as Cl_2,O_2, SO_2, CH_4 etc. The formation of an outermost eight-electronic layer as the result of chemical combination has given rise to the name of the *Octet Theory of Valency* as was first developed by Lewis and Langmuir, since an outermost layer of eight electrons is a characteristic feature of the atoms of the rare-gas elements. Each electrovalent bond consists in the transfer or acceptance of an electron by the atom; the atoms which transfer or part with elctrons are therefore called *electropositive* and those which receive the electron are termed *electronegative*. Each co-valent bond consists

in the sharing of a pair of electrons. Co-valencies are again subdivided into *normal co-valency* and *co-ordinate co-valency* according to Sidgwick. In normal co-valency each atom contributes one electron to the shared pair and in the co-ordinate co-valency both the shared electrons come from one of the combining atoms. This latter is assumed to explain the formation of complex ions and compounds of the Werner-type.

This modern electronic theory of valency, though capable of offering a satisfactory explanation for a large variety of chemical combinations and even predicting the course of the reaction in certain spheres of organic chemistry, is yet far from attaining its perfection. Instances are not rare where it signally fails. Some of these exceptions will be discussed presently.

We can classify our chemical compounds under two main heads.

1. Compounds of the first order or the so-called simple compounds. This includes the organic compounds as well.

2. Compounds of the second order which can again be sub-divided into—

(*a*) Double salts and hydrates, and
(*b*) Complex salts.

Among the compounds of the first order we have got both homo-polar and hetero-polar compounds characterised by the manifestation of co-valency and electro-valency. Exceptions that can be cited under this head are—

$$SF_6,\ PF_5,\ PCl_5,\ BrF_3,\ IF_5,\ B_2H_6,KI_3.$$

Some of these cases, as is well known, have long attracted the attention of the workers in this field; and several suggestions have been made to explain the mechanism of their formation. But it must be admitted that they have failed to improve the situation. The cases of sulphur fluoride and phosphorus halides have long been thoroughly discussed. And unless we assume them to be hetero-polar with sulphur as a hexavalent positive ion and phosphorus as a pentavalent one, which cannot be justified from the behaviour of the substances themselves, there is no other way of representing them on the basis of the electronic theory of valency. The case of boron hydride is still an unsolved problem in spite of numerous electronic constitutions suggested for it. The cases of BrF_3 and IF_5 are still in a worse position. Their formation can in no way be accounted

for either on the basis of electro-valency or co-valency. Why should bromine or iodine atom with seven peripheral electrons should part or share with three or five more electrons is beyond any reasonable explanation. The fluorine molecules, on the other hand, can never be made to attach themselves to a fluorine atom with its completed octet on the basis of our modern hypothesis. The same difficulties are met with in the case of I_3-ion as well.

Evidently considerations of some other factors besides the sharing or transfer of electrons must be made in order to explain the mechanism of chemical combination. Whether it is of the nature of an electrostatic or magnetic attraction, we are not yet in a position to affirm. Study of the molecular structure by the physicists, it is hoped, will furnish us ere long with the solution of all these difficulties.

Passing on to the compounds of the second order—the hydrates and the double salts—we encounter the same difficulties again. Why should KCl, $MgCl_2$ and H_2O molecules which according to modern hypothesis all possess stable and completed structure, combine again to form a complicated molecule known as carnallite $KCl,MgCl_2$, $6H_2O$ cannot be easily explained unless we assume some sort of electrostatic attraction between the ions.

Finally the so-called complex compounds of the Werner-type present entirely a new aspect of the problem. Here unlike in double salts and hydrates, we find that the properties of the component molecules undergo a profound modification in the complex formed just as we meet with in the case of the compounds of the first order. It must be noted here however that there is no sharp demarcation between the complex and the double salts. The transition between them is gradual and insensible. Even among the well-known complexes we find different degree of stability. Some are quite stable in solution, the others are not. The most charcteristic complex compounds are formed by the elements of the transitional group of the Bohr's periodic system. Even these exhibit a great difference in properties. For example, whereas the simple cobaltous and cobaltic salts are strongly paramagnetic, the complex cobaltic salts on the other hand, are diamagnetic. Simple nickel salts and most of the complex nickel salts possess almost the same paramagnetic susceptibility. But there are certain complex nickel-compounds such as $K_2Ni(CN)_4$, nickel-dimethylglyoxi e and nickel-dicyandiamidine which are diamagnetic.

Evidently here also we find indications of the existence of two types of complex compounds. One of my colleagues in my laboratory has named them "perfect" and "imperfect complexes." The question now arises—does this indicate two different types of combination? It has already been stated that a co-ordination bond like a co-valent bond is due to the sharing of a pair of electrons between the co-ordinating ion and each co-ordinated partner only with this difference that in a co-ordination bond both the electrons of the pair come from the co-ordinated atom. Again the number of co-ordination valency, or co-ordination number as it is called, that an atom usually manifests is either four or six. What determines this number is not quite clear. According to Magnus it is the size and the charge of the central co-ordinating ion which regulate this number assuming that the ions or atoms are spherical in shape. The larger is the size of the co-ordinating atom the larger is its co-ordination number as it can accommodate larger number of co-ordinated partners around its surface.

Suggestions have also been made by Welo, Baudisch, and others that in the formation of complex compounds the central co-ordinating atom tends to assume the next inert gas configuration by accepting electrons from the co-ordinated partners. This holds good only in the cases of cobaltic, iridic, rhodic and platinic complexes and in certain ferrous, molybdenum and tungsten complexes. Thus:

	Electron number.	Co-ordination number.	Total electron.
Co^{3+}	24	6	36 (Krypton structure)
Ir^{3+}	74	6	86 (Niton ,,
Pt^{4+}	74	6	86 ,, ,,
Rh^{3+}	42	6	54 (Xenon ,,
Fe^{2+} (ferrocyanides)	24	6	36 (Krypton ,,
Mo^{4+} (molybdicyanides)	38	8	54 (Xenon ,,
W^{4+} (tungsticyanides)	70	8	86 (Niton ,,

Each co-ordination number or bond supplies two electrons as has already been stated.

Curiously enough all these complexes which thus assume the inert-gas structure are diamagnetic. All the other complexes formed

by nickel, ferric iron, chromium, palladium, osmium, manganese, tri- and penta-valent molybdenum and tungsten, bivalent platinum, bivalent cobalt, etc., fail to comply with this requirement (formation of inert-gas structure).

It has already been pointed out that the complexes can be conveniently classified into "perfect" and "imperfect" types. It may be assumed as one of my colleagues has already done that in the "perfect" type actual sharing of electrons takes place forming the so-called co-ordination bonds. In the "imperfect" type which may be regarded as forming the transition between the "perfect" complexes and the double salts, the bond is due to some sort of electrostatic or electromagnetic attraction between the co-ordinating atom and the co-ordinated partners which usually possess a dipole moment.

In this connection one may enquire why only some of the members of the transitional elements are peculiarly suited for the formation of complex compounds. Why among the neighbouring elements Cr, Mn, Fe, Co, and Ni,—it is Co and Cr and to certain extent Fe and Ni that easily form complexes? In manganese however this property of complex building is only very slightly developed. Further it is known that boron forms stable boron trifluoride and boron trichloride. But whereas boron trifluoride easily combines with HF and metallic fluorides to form quite stable complex fluoborates, boron trichloride fails to manifest any such capacity to combine with hydrochloric acid and chlorides. Similarly potassium silicofluorides and potassium titanifluorides represent quite stable complexes whereas the corresponding chlorides are unknown This difference of behaviour between chlorine and fluorine is inexplicable. This and several other similar difficulties still await a satisfactory explanation.

Further there are many so-called complex salts which are known only in the solid condition. They break up as soon as they pass into aqueous solution. We, therefere, find that the strength of the valency-bond gradually diminishes as we pass from the simple compounds to complex and double salts. And we may reasonably assume that this finally degenerates or weakens into the so-called lattice-force in the crystal structure. The molecules in the crystal are held together by a force which vanishes rapidly as the crystal either passes into the solution or melts or if it sublime into gaseous condition. The only attractive force between

the molecules in the latter conditions is what is known as Van der Waal's attraction. It is not difficult to perceive a qualitative unity in this diverse manifestation of attractive or combining forces ranging between Van der Waal's attraction at the one end and the sharing or transfer of electrons at the other. Many of the so-called absorption-compounds represent the transition between the true chemical combination and physical agglomeration.

Finally the case of a type of compounds known as intermetallic compounds may be here conveniently discussed. In a true metallic element the binding between the atoms is neither polar nor unpolar. It seems to represent a transition between the two. The metallic atoms possess a strong tendency to part with their outermost loosely-bound electrons and thus become positive ions of stable configuration. When two such atoms approach each other, the loosely-bound valence-electrons of both tend to leave their original owners ; but as neither of the combining atom would tolerate any excess of electrons in their own sphere, these binding electrons simply vibrate between the two atomic cores. They cannot enclose the nuclei of the combining atoms as in homopolar bindings. This differentiates the metallic binding from co-valency. In the formation of true intermetallic compounds therefore we do not meet any valence-regularity. Compounds of composition are formed which do not correspond to our usual valence-conception of the combining atoms. Compounds of the type Cd_5Na, Ca_4Zn, $LiHg_3$, $NaHg_4$, etc., are not rare among them. Evidently quite different factors dominate the formation of true inter-metallic compounds. It appears that the size of the atoms determines more or less the nature of the compounds formed. We shall see later on that the same volume-factor also determines to a great extent the crystal-form built by the elements and compounds. Consequently the binding force in the inter-metallic compounds resembles what prevails between the building stones of a crystal unit.

Only in those cases where there is a sensible polar difference between the partners of intermetallic compounds conditions of valency are found to be fulfilled, *e.g.*, in Ag_3Sb, As_2Cd_3, etc.

We have so long discussed the chemical properties of the elements and compounds and have sought to trace the cause and origin thereof. The question that naturally arises next is what determines the physical properties of the elements and their compounds. Just as

in the case of the chemical properties the outermost valency-electrons are also responsible for the physical properties of the atoms. But, strictly speaking, it is the size or volume of the atom or the ion that mainly determines these properties. Of course the volume of the atom is related to the position of the valency electrons. The properties of diffusion, refraction, crystal-form, ionisation potential and isomorphous replacibility are closely connected with the atomic or ionic radii. Of all these, I shall confine myself only to the crystal-form and isomorphous replacibility, being the most important physical properties from the chemist's point of view.

Goldschmidt who has been working on crystal-chemistry for several years and to whom we are indebted for the signal advancement in this branch of science, sums up the determining factors in crystal-formation in the following words:

"The structure of a crystal is determined by the ratio of numbers, the ratio of sizes and the properties of polarization of its building stones. As the building stones of crystals we visualise atoms, ions or groups of atoms."

By polarization is meant the deformation of the electronic orbits of the anion by the cation which undoubtedly affects the volume relationship.

Mitscherlich's law of isomorphism, which had played such an important part in the development of our science specially regarding the determination of atomic weights, finds an easy explanation in the light of above conclusions. Mitscherlich discovered that two substances which are homeomorphous and form mixed crystals are isomorphous and possess analagous chemical formulae. Its explanation is now quite clear. But the reverse is not always true, *i.e.*, all substances having the same type of chemical formulæ are not isomorphous; because, as Goldschmidt has deduced, analogy is required not only as to the numbers but also as to the "properties" of particles such as the relative size and properties of polarisation.

Isomorphism is primarily related to the atomic or ionic volume and many puzzling and anomalous cases of isomorphism observed by Barker, Goldschmidt and others have now been easily explained. I shall here deal with one very interesting case of isomorphism which was noticed by Barker but has recently been thoroughly worked out in all details in my laboratory by two of my colleagues. I mean the isomorphism of fluoberyllates and sulphates. It has been shown that all fluoberyllates form mixed crystals with their corresponding

sulphates. The analogy extends even to the double sulphates. The following fluoberyllates have been prepared and studied by them:

A_2BeF_4 where A = NH_4, Li, Na, K, Rb and Cs isomorphous with corresponding sulphates. $(NH_4)_2BeF_4 \cdot M_2SO_4 \cdot 6H_2O$ and $(NH_4)_2BeF_4 \cdot M_2BeF_4 \cdot 6H_2O$ isomorphous with $(NH_4)_2SO_4 \cdot M_2SO_4 \cdot 6H_2O$, where M = Ni, Co, Zn, Mn, Cd, Cu, Fe″ and Mg.

Now if we assume that sulphur atom in SO_4 is hexavalent and positive, beryllium in BeF_4 is bivalent and positive then we find that their ionic radii according to Goldschmidt are exactly identical being equal to 0·34A°. Similarly fluorine ion and oxygen ion have ionic radii equal to 1·33A° and 1·32A° respectively. Further the number of particles in the two complex radicles is the same and the nature and value of their charges are also the same. Hence it can be easily expected from Goldschmidt's principle that they will exhibit close isomorphous relationships. It has further been shown that the analogy between these two types of compounds extends to many other physical properties due to their isosteric and isoelectric nature.

The isomorphous replacibility of K and Rb by (NH_4), isomorphism of KNO_3 and $CaCO_3$, LiF and MgO, and of KBF_4 and $KClO_4$ can also be accounted for on the same basis. In ammonium ion we find a radicle possessing isomorphous relationships with metallic ions like K and Rb. This has been possible because their ionic radii are very much alike.

So we are now in a position to affirm that the physical properties of the elements and compounds are mostly determined by the relative sizes of their atoms or the corresponding ions.

In this brief discussion I have attempted to indicate the recent progress in our knowledge of the properties of chemical elements and compounds. And in conclusion I would like to express our indebtedness for many of the recent advancements in this branch of our science to our non-chemist colleagues—specially the physicists who have been able to establish on a firm and theoretical basis many of our empirical assumptions and hypotheses.*

* For many of the ideas elaborated in this paper I am deeply indebted to Mr. P. B. Rây of the University College of Science, Calcutta.

Studies in Azomethine Azo-Dyes.[1]

By Rajendra Nath Sen and (the late) Akshoy Kumar Sen.

From a study of the tinctorial properties of a series of azomethine azo-dyes—containing a single azomethine group in the *para*-position to the azo-group but without any auxochromic group in the molecule—prepared by Green and Sen (*J. Chem. Soc.*, 1912, **97**, 2242), it was found that the shade of an azo-dye remains practically unaltered by the introduction of an azomethine group.

The present work has been undertaken for further studies in azomethine azo-dyes in respect of (1) the effect of introducing an additional azomethine group in the *para*-position to the azo-group, and (2) the effect of an auxochrome (OH) in the *para*-position to the azo-group.

A dialdehyde, *viz.*, azo-benzaldehyde-sulphonic acid [$CHO{\cdot}C_6H_3(SO_3H){\cdot}N_2{\cdot}C_6H_3(SO_3H){\cdot}CHO$] obtained from "Mikado orange"

$$\begin{matrix} CH{\cdot}C_6H_3(SO_3Na){\cdot}N_2{\cdot}C_6H_3(SO_3Na)CH \\ \| \qquad\qquad\qquad\qquad\qquad\qquad \| \\ CH{\cdot}C_6H_3(SO_3Na){\cdot}N_2{\cdot}C_6H_3(SO_3Na)CH \end{matrix}$$

in the manner described by Green and Leonhardt (*J. Chem. Soc.*, 1906, **86**, 1613) was selected for the preparation of dyes, containing two azomethine groups in the *para*-positions to the azo-group but without any auxochromic group in the molecule. The dialdehydic nature of the compound has been fully investigated and established in this work, and by its condensation with different amino-compounds and several dyes containing free amino-groups, the first type of dyes has been obtained.

The condensation products of the dialdehyde with several monoamines, such as aniline, α-naphthylamine and β-naphthylamine, produce on wool shades (varying from yellow to brown) considerably lighter than the shade (orange) obtained with the dialdehyde. This shows that the introduction of two azomethine groups makes the colour lighter. This appears to be in perfect

[1] The delay in the publication of the paper is due to the sudden death of one of the authors.

agreement with the conclusion arrived at by Sen and Sett (*J. Amer. Chem. Soc.*, 1924, **46**, 111) namely, that too much multiplication of chromophores tends to make the colour lighter. The compounds in the solid state possess colour from yellow to reddish brown and give differently coloured solutions in strong sulphuric acid. The aniline compound gives a yellowish-red solution, the α-naphthylamine compound a reddish-brown solution and the β-naphthylamine compound gives a dark-brown solution, whereas the dialdehyde itself gives an orange-red solution.

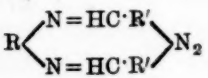
The presence of free amino-groups in the condensation product (I) of the dialdehyde with semicarbazide is confirmed by the evolution of nitrogen by the action of nitrous acid. It dyes wool in golden-yellow shade which is lighter than that (orange) produced by the dialdehyde. The compound possesses a yellow colour and gives a yellowish-red solution in concentrated sulphuric acid.

$$H_2N{\cdot}CO{\cdot}NH{\cdot}N{=}HC{\cdot}R'{\cdot}N_2{\cdot}R'{\cdot}CH{=}N{\cdot}NH{\cdot}CO{\cdot}NH_2$$

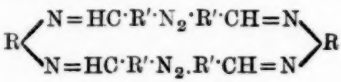
$$(R' = C_6H_3{\cdot}SO_3H)$$

(I)

The absence of any free amino- or any free aldehyde group in the condensation products of the dialdehyde with the diamines namely hydrazine, *o*-phenylene diamine, *p*-phenylene diamine and benzidine, indicates that the aldehyde and the diamine react in molecular proportions with the elimination of two or four molecules of water, giving rise to polymembered ring structures (II or III).



(II)

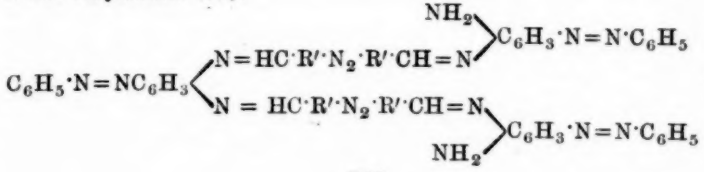


(III)

Such ring structures are supported by a recent work of Adams, Bullock and Wilson (*J. Amer. Chem. Soc.*, 1923, **45**, 521). The general properties, such as extreme insolubility, and high melting points referred to in that work, are very similar to those of the condensation products of benzidine and *p*-phenylene diamine with the azo-aldehyde. The molecular weight could not be determined owing to the great insolubility of the compounds, and for the sake of simplicity the structure (II) has been given.

The colour of the compounds obtained by condensing *p*-phenylene diamine and benzidine with the dialdehyde is almost the same, although one contains a phenyl and the other a diphenyl residue. The behaviour of the two compounds towards concentrated sulphuric acid is however interesting. The benzidine compound dissolves in sulphuric acid with a violet colour, but on dilution with water a red precipitate is thrown down and the solution becomes colourless ; whilst the *p*-phenylene diamine compound produces a red colour in concentrated sulphuric acid, which on dilution changes to light-violet. It is very difficult to study the dyeing properties of these compounds owing to their insolubility and ready tendency to hydrolyse. The compound obtained from hydrazine gives a red solution in sulphuric acid and dyes wool in orange shade, while the compound obtained from *o*-phenylene diamine dyes wool in fine canary yellow shade and dissolves in concentrated sulphuric acid with yellowish-red colour. The deepening of colour in the hydrazine compound is presumably due to the presence of the aldazine group (−CH=N−N=CH—).

The dialdehyde has further been condensed with several dyes (containing free amino-groups) such as safranine, rosaniline and chrysoidine and in every case the colour becomes lighter than that of the original dye. The reactions with safranine and rosaniline are found to occur in molecular proportions and the usual ring formation is also supported in these cases by the absence of free amino- and CHO groups. It is interesting to note that in the case of chrysoidine (with two amino-groups in *meta*-position) two molecules of the aldehyde react with three molecules of the chrysoidine (IV).



(IV)

In this connection a noteworthy observation has been made that the dyes rosaniline and safranine can be estimated quantitatively by titrating with a standard solution of the dialdehyde, using phenylhydrazine acetate solution as an external indicator.

With a view to study the effect produced on azomethine azo-dyes by the presence of an auxochromic group (OH), a monoazo-aldehyde with an OH-group in the *para*-position to the azo-group, *viz.*, salicylazobenzaldehyde-sulphonic acid [CHO· C_6H_3 (SO_3H) N_2·C_6H_3·(OH) COOH] has been prepared from 'Hessian yellow.'

$$\begin{array}{l} CH{\cdot}C_6H_3(SO_3Na){\cdot}N_2{\cdot}C_6H_3(OH){\cdot}COOH \\ \| \\ CH{\cdot}C_6H_3(SO_3Na){\cdot}N_2{\cdot}C_6H_3(OH){\cdot}COOH \end{array}$$

A few compounds were obtained by the condensation of the monoazoaldehyde with amino-compounds. By way of comparison it may be noted that they produce on wool similar shades as those obtained from the corresponding compounds of phenetoleazobenzaldehyde-sulphonic acid (Green and Sen, *loc. cit.*)

Thus from a study of the compounds described in this paper, it is found that in azomethine azo-dyes—(1) the effect of introducing an additional azomethine group in the *para*-position to the azo-group lightens the colour more or less, except in the case of two azomethine groups in juxtaposition, constituting the aldazine group which deepens the colour ; (2) the presence of an auxochromic group (OH) in the *para*-position to the azo-group, like the auxochrome in the *para*-position to the azomethine group (previously studied by Green and Sen) has practically no effect.

Experimental.

(A) *Sodium* p : p'-*Dialdehydo-azobenzene*-m : m'-*disulphonate.*

To a filtered solution of "Micado orange" (40 g.) in boiling water (2·5 litres), cooled to 0—5°, a 3% solution of potassium permanganate (2·36 g.) is added gradually until a permanent pink colour is obtained, the solution being mechanically stirred during the addition. After the reaction is complete the solution is boiled, filtered from the manganese dioxide sludge and the residue repeatedly extracted with hot water. After neutralisation by hydrochloric acid, the combined filtrates are concentrated to a small bulk on the water-bath and the sodium salt of the sulphonic acid precipitated by the addition of common salt. The sodium salt is collected, washed with

alcohol (50%) and purified by crystallisation from dilute alcohol, when it is obtained in buff-coloured microscopic needles. A further quantity of less pure material can be obtained by the further addition of common salt to the original filtrate (yield, 67·5%). The disodium salt is readily soluble in water and the sulphonic acid is not precipitated by the addition of acid. On treatment with phenylhydrazine it yields a reddish-brown phenylhydrazone. It dissolves in sulphuric acid yielding an orange-red solution which on dilution becomes orange and finally yellow. It dyes wool an orange shade. (Found: N, 6·29, 6·34; S, 14·65, 14·77. $C_{14}H_8O_8N_2S_2Na_2$ requires N, 6·33 ; S, 14·48 per cent.).

The *barium salt* is insoluble in cold water and slightly soluble in hot water. (Found : Ba, 25·91, 25·94; N, 5·17, 5·20. $C_{14}H_8O_8N_2S_2Ba$ requires Ba, 25·75; N, 5·24 per cent.).

A determination of the aldehyde groups is effected by titrating with a standard solution of phenylhydrazine hydrochloride in presence of sodium acetate, employing phenetoleazobenzaldehyde-sulphonic acid as an external indicator. (Found : CHO, 13, 12·8. $C_{14}H_8O_8N_2S_2Na_2$ requires CHO, 13·12 per cent.).

Preparation of the Azomethine Azo-dyes.

(1) *Condensation product with semicarbazide* is prepared in the usual manner and is crystallised from hot water. It is a yellow substance, moderately soluble in cold water, soluble in concentrated sulphuric acid with a yellowish-red colour which changes to yellow on dilution ; it dyes wool in golden-yellow shade. (Found : N, 20·09, 19·98. $C_{16}H_{14}O_8N_8S_2Na_2$ requires N, 20·14 per cent.).

(2) *Condensation product with aniline.*—A hot solution of aniline (1·4 c.c.) in dilute acetic acid is slowly added to a hot aqueous solution of the aldehyde (3 g.), the mixture being stirred all the time and the reaction completed by warming for a short time. The yellow precipitate, thus obtained, is filtered off, washed with dilute acetic acid and is crystallised from hot water. It is a yellow powder, sparingly soluble in cold water, soluble in concentrated sulphuric acid with a yellowish-red colour, which changes to yellow on dilution ; dyes wool a yellow shade. (Found: N, 9·57, 9·64, $C_{26}H_{18}O_6N_4S_2Na_2$ requires N, 9·46 per cent.).

Other condensation products with the mono-amines are listed in Table A.

(3) *Condensation product with benzidine.*—To a cold acidified aqueous solution of the aldehyde (4 g.) a solution of benzidine (1%) in hydrochloric acid is slowly added till the solution is almost colourless, when a dark-brown precipitate separates in the cold. The precipitate is filtered off, thoroughly washed with dilute hydrochloric acid, then with hot water and hot alcohol and dried ; the free compound, thus obtained, is dark-brown, insoluble in hot water, slightly soluble in caustic alkalis, practically insoluble in hydrochloric acid, which hydrolyses the compound on heating. It is sparingly soluble in alcohol and practically insoluble in other organic solvent, soluble in concentrated sulphuric acid with a violet colour and on dilution a red precipitate is thrown down; it dyes wool a brownish-yellow shade. (Found : N, 10·03, 9·89. $C_{26}H_{18}O_6N_4S_2$ requires N, 10·25 per cent.).

Other condensation products with the diamines are listed in Table A.

(4) *Condensation product with chrysoidine.*—A hot aqueous solution of the aldehyde (4 g.) is added drop by drop to a solution of chrysoidine (3 g.) in dilute hydrochloric acid, heated to 70-80°. The solution is then vigorously stirred until it is cold. The precipitate, thus obtained, is filtered, washed with hot water and hot alcohol; the free compound, thus obtained, is a scarlet powder, insoluble in water and in acid, slightly soluble in caustic alkalis. It dissolves in concentrated sulphuric acid with a scarlet-red colour changing to reddish-orange on dilution; it dyes wool a yellow shade. (Found: N, 16·26, 16·31 ; S, 9·32. $C_{64}H_{48}O_{12}N_{16}S_4$ requires N, 16·47; S, 9·40 per cent.).

Condensation products with safranine and rosaniline are listed in Table A.

(B) *Sodium Salicylazobenzaldehydesulphonate.*

It was prepared by the oxidation of a solution of ' Hessian yellow ' (Merck) (30 g.) in water (3 litres) with potassium permanganate solution (3% , 6·6 g.) in the manner described in the preparation of the dialdehyde. The isolation and the purification of the compound was similarly carried out (yield, 70%). The free compound, obtained as reddish-orange microscopic needles by crystallising the sodium salt from hot water acidified with hydrochloric acid, is moderately soluble in cold water. It reacts very easily with phenyl-

hydrazine producing an orange phenylhydrazone. It dissolves in concentrated sulphuric acid with a red colour, which on dilution changes to yellow ; sodium hydroxide solution produces a deep red colouration ; it dyes wool an orange (slightly yellowish) shade. (Found: N, 7·96, 8·04 ; S, 9·24. $C_{14}H_{10}O_7N_2S$ requires N, 8·0; S, 9·14 per cent.).

A determination of the aldehyde group is effected in the manner described in the case of the dialdehyde. (Found : CHO, 8·19, 8·27. $C_{14}H_{10}O_7N_2S$ requires CHO, 8·29 per cent.).

The azomethine azo-dyestuffs prepared from the mono-aldehyde are listed in Table B.

TABLE A.

Formula.	Preparation.	Analysis. Found. %	Analysis. Calc. %	Shade on wool.	Properties.
(5) $C_{24}H_{22}O_6N_4S_2Na_2$	Aqueous solution of the dialdehyde (3 g.) + alcoholic solution of β-naphthylamine (1·9 g.) on the water-bath.	N, 8·0, 8·01	N, 8·09	Greyish-orange.	Crystallised from dilute alcohol; a bright orange powder, moderately soluble in cold water, soluble in conc. sulphuric acid (dark-brown solution).
(6) $C_{24}H_{24}O_6N_4S_2$	Aqueous solution of the dialdehyde (2·21 g.) + a solution of α−naphthylamine (1·43 g.) in dilute hydrochloric acid on the water-bath.	N, 8·54, 8·62	N, 8·64	Brown.	Crystallised from dilute alcohol; the free compound is reddish-brown, slightly soluble in hot water, readily in alcohol.
7) $C_{30}H_{18}O_6N_4S_2Na_2$	The dialdehyde (3·31 g.) + o-phenylene diamine (·8 g.) + glacial acetic acid on the water-bath.	N, 10·86, 10·82	N, 10·89	Fine canary yellow.	Crystallised from dilute alcohol; yellow powder with a slight orange tinge; sparingly soluble in cold water, soluble in conc. sulphuric acid (yellowish-red, changing to yellow on dilution).
(8) $C_{30}H_{14}O_6N_4S_2$	By mixing molecular proportions of acidified solution of the dialdehyde and o-phenylene diamine in the cold.	N, 11·81, 11·72	N, 11·91	Chocolate.	Reddish-brown free compound, insoluble in water, slightly soluble in caustic alkalis, sparingly in hot alcohol, soluble in concentrated sulphuric acid (red, changing to violet on dilution).

TABLE A (*continued*).

Formula.	Preparation.	Analysis. Found. %	Analysis. Calc. %	Shade on wool.	Properties.
(9) $C_{14}H_8O_8N_4S_2Na_2$	Aqueous solution of hydrazine sulphate (0·64 g.) and dialdehyde (2·3 g.) on the water-bath.	N, 12·74, 12·66	N, 12·79	Bright orange.	Deep orange sodium salt, fairly soluble in cold water, soluble in concentrated sulphuric acid (red, changing to yellow on dilution).
10) $C_{33}H_{22}O_6N_8S_2$	The dialdehyde + rosaniline hydrochloride in the same manner as in (4).	N, 10·44, 10·46	N, 10·7	Bluish-red.	The free compound has a deep chocolate colour, moderately soluble in hot water, easily soluble in alcohol, soluble in concentrated sulphuric acid (brownish-red).
(11) $C_{34}H_{26}O_7N_6S_2$	The dialdehyde + safranine in the same manner as in (4).	N, 12·34, 12·26	N, 12·10	Red.	The free compound is a chocolate-coloured powder, moderately soluble in hot water and in alcohol.

TABLE B.

	Formula.	Preparation.	Analysis. Found. %	Analysis. Calc. %	Shade on wool.	Properties.
(1)	$C_{20}H_{12}O_6N_2S$	The aldehyde + aniline acetate.	N, 9·85, 10·06	N, 9·88	Fast yellow.	Yellow powder, readily soluble in alcohol, sparingly soluble in cold water.
(2)	$C_{40}H_{28}O_{12}N_6S_2$	The aldehyde + benzidine hydrochloride.	N, 9·83, 9·94	N, 9·91	Yellow.	Reddish-orange powder, slightly soluble in water and moderately in hot alcohol.
(3)	$C_{49}H_{30}O_{12}N_8S_2$	The aldehyde + chrysoidine hydrochloride.	N, 12·88, 12·89	N, 12·78	Yellow.	Red colour, slightly soluble in water, easily soluble in hot alcohol.
(4)	$C_{47}H_{33}O_{12}N_7S_2$	The aldehyde + rosaniline hydrochloride.	N, 10·14, 10·23	N, 10·29	Bluish-red.	Deep chocolate colour, sparingly soluble in cold water, freely soluble in hot alcohol.
5)	$C_{46}H_{34}O_{12}N_8S_2$	The aldehyde + safranine hydrochloride.	N, 11·32, 11·34	N, 11·23	Red (slightly orange).	Chocolate colour, slightly soluble in hot water, but more soluble in alcohol.

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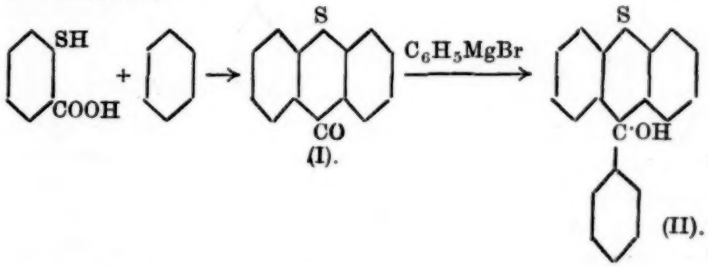
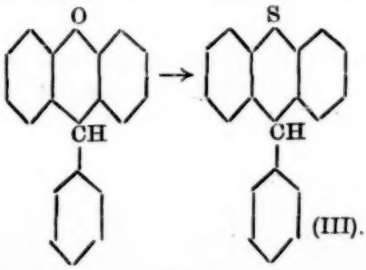
Studies in Sulphur-containing Dyestuffs. Part I. Derivatives of Alkyl and Aryl Sulphido-diphenylmethane.

By Mangesh V. Betrabet and Gopâl Chandra Chakravarti.

No direct synthesis of phenylthioxanthenes seems to have been attempted or accomplished. An important method by which phenylthioxanthanols (II) have been prepared is by the action of magnesium phenylbromide upon thioxanthones (I), (Davis and Smiles, *J. Chem. Soc.*, 1910, **97**, 1296 ; Gomberg and Cone, *Annalen*, 1910, **376**, 201) :—



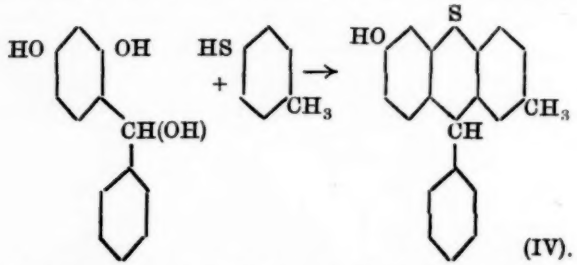
But even by this method no dyestuff containing auxochromes in the phenyl groups of the thioxanthene residue has been synthesised and therefore these thioxanthenes being colourless are useless in practical dyeing. Another method for the preparation of these compounds, by the action of sulphur sesquioxide upon phenylxanthene and its derivatives, has been described (D.R P. 65739/1892).



Pope and Howard (*J. Chem. Soc.*, 1910, **97**, 78) devised a very

simple and interesting synthesis of phenylxanthenes by condensing 2:4-dihydroxybenzhydrol with phenol and substituted phenols, and also of phenylacridines and pyronines by condensing the same hydrol with aromatic amines and aminophenols respectively (Pope and Howard, *ibid*, 1910, **97**, 972).

We attempted to bring about a similar condensation between the hydrol and aromatic mercaptans with the object of directly synthesising the phenylthioxanthenes by employing a suitable condensing agent. The reaction was expected to proceed as follows:—

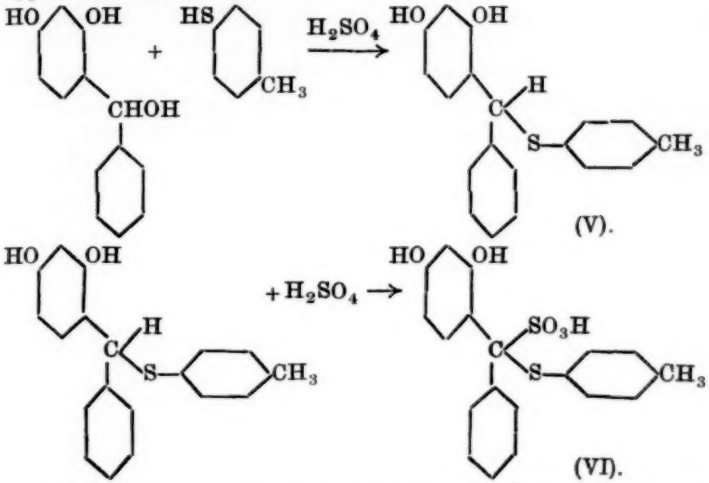


(IV).

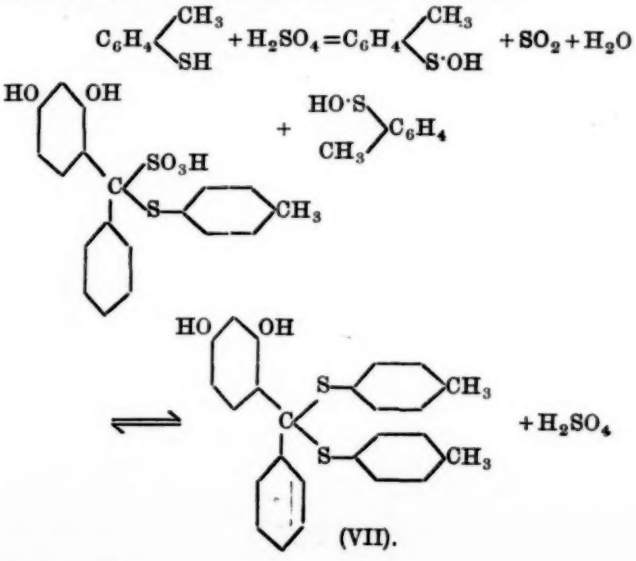
When fused zinc chloride was used as the condensing agent, highly insoluble red substances containing zinc in the molecules were invariably obtained, from which the zinc could not be removed by any means. Although these products were found to contain sulphur they were not further investigated on account of the difficulty in their purification and the indefiniteness of their composition. With fused sodium acetate also the desired results could not be obtained. Phosphorus pentoxide could not be used as the 2:4-dihydroxybenzhydrol is insoluble in inert solvents like benzene, xylene, etc. Concentrated sulphuric acid, however, brought about the condensation between aromatic mercaptans and benzhydrol and its derivatives. But the products of the reaction proved to be entirely different from those anticipated. Generally two types of compounds were isolated: (A) *Acidic*, considerably soluble in hot water, alcohol and alkali carbonate solutions: (B) *Neutral*, insoluble in water and most other solvents except pyridine and sometimes alcohol.

The absence of mercaptanic properties in any of these condensation products indicated that the hydrogen of the mercaptanic group enters into the reaction. Moreover, the solubility of A-class of compounds in hot water as well as in alkaline carbonate solutions with the evolution of carbon dioxide suggested the replacement of

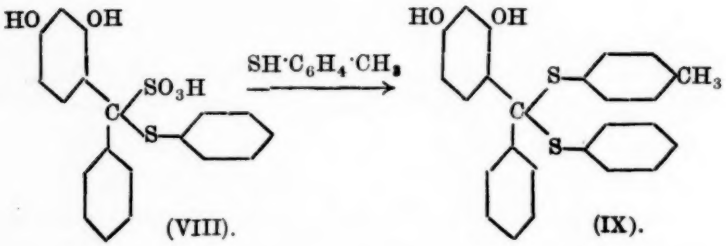
a hydrogen atom, preferably the methine one (V), by a sulphonic acid group. The mechanism of the reaction in this condensation appears to be as follows:—



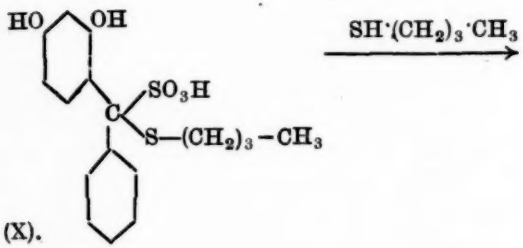
The simultaneous production of the neutral substances (class B) which are always attended with considerable evolution of sulphur dioxide should therefore be represented as below:—



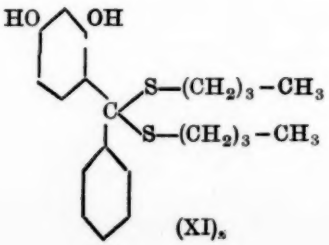
In the above formulæ an assumption has been made that the sulphonic acid is the intermediate product. To verify this the sulphonic acid (VI) was treated with an equivalent quantity of *p*-tolylmercaptan in the presence of concentrated sulphuric acid. It was found that this reaction gave 30-40% of the disulphide (VII). This is quite in accordance with the view adopted. Moreover, the mechanism suggested above, would not only render the synthesis of a disulphide containing two different mercaptanic radicle (IX) possible; but also enable the formation of compounds possessing aliphatic (XI) as well as mixed aliphatic and aromatic (XII) radicle. All these expectations have been realised.



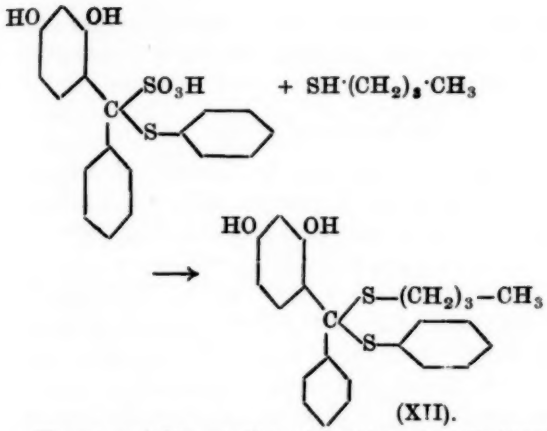
(VIII). (IX).



(X).



(XI).



(XII).

The poor yields of the disulphides in all these condensations suggested that we are dealing with a balanced chemical reaction. That this was the case was proved from the fact that when the pure disulphide (VII) was similarly treated with concentrated sulphuric acid, the original sulphonic acid (VI) was regenerated. These two reactions mentioned above further definitely establish the position of the sulphonic acid group in the molecules.

In this paper the condensation products of benzhydrol, 2:4-dihydroxybenzhydrol and 2:4-dihydroxy-4′-methoxybenzhydrol with phenyl mercaptan, *p*-tolylmercaptan, benzyl hydrosulphide and butyl hydrosulphide are described.

The diphenyl-aryl-sulphido-methane sulphonic acids are more coloured than the diphenyl-aryl-disulphido-derivatives. Both of them are red in colour, but dye wool in slightly different shades. The former give a buff-coloured shade while the latter give fawn-coloured shades to wool. A very slight difference in shade is evidenced with a change in the mordant. They dye wool directly but not cotton. The difference in colour between diphenyl-alkyl-sulphido-methane-sulphonic acids and the corresponding disulphide derivatives is very little. Mostly they are deep brown in colour and dye wool in slightly deeper fawn-coloured shade. It has also been observed that unsubstituted diphenyl-aryl-sulphidomethanes are much less coloured. They are faintly brick-red in colour. The potassium salts of these compounds are deep red.

By using freshly prepared zinc chloride having dry hydrochloric acid gas in occlusion, the desired condensation between the

hydroxybenhydrols and substituted phenyl mercaptans has been subsequently realised by us and will form the subject matter for a further communication.

Experimental.

Benzhydrol was prepared according to the method described by Marvel and Hansen ("Organic Syntheses," Vol. VIII, 24) and 2:4-dihydroxy- and 2:4-dihydroxy-4'-methoxybenzhydrols were prepared by the method of Pope and Howard (*loc. cit.*).

Condensation of 2:4-*Dihydroxybenzhydrol with* p-*Tolyl Mercaptan.*—2:4-Dihydroxybenzhydrol (4 g.) was added in small quantities to a mixture of concentrated sulphuric acid (25 c.c.) and *p*-tolyl-mercaptan (6 g.), and shaken well over a period of two hours. The mixture was allowed to stand overnight at room temperature, then heated on a water-bath for one hour and poured over crushed ice and excess of water. The product was filtered and washed thoroughly with ice-cold water and dried on a porous plate. It was a pasty red mass and presented great difficulties in purification. After repeated extraction with hot benzene and ether, it was obtained in a powdery form. This powder partially dissolved in hot 5% sodium carbonate solution. It was filtered and a residue (A) was obtained. The filtrate was neutralised with dilute hydrochloric acid solution, cooled in ice and the precipitate filtered and washed thoroughly with cold water. Then it was crystallised from alcohol. *α-(p-Tolylmercapto)-2:4-dihydroxy diphenylmethanesulphonic acid* (VI) was obtained as a dark-red, granular micro-crystalline substance, m.p. 150-159°. (Found: C, 59·3 ; H, 4·86 ; S,* 15·6. $C_{20}H_{18}S_2O_5$ requires C, 59·7 ; H, 4·48 ; S, 15·9 per cent.).

The *potassium salt* was prepared by adding a saturated solution of potash in absolute alcohol to the sulphonic acid and diluting with water till the whole thing went into solution on warming. Excess of absolute alcohol was then added to precipitate the potassium salt. This was filtered and washed well with absolute alcohol to remove the free potash. It was then dried and obtained as a red crystalline powder. (Found: K, 22·3. $C_{20}H_{15}S_2O_5K_3$ requires K, 22·2 per cent.).

* These compounds are only partially oxidised by nitric acid in the carius' tube. So the estimation of sulphur was carried out by further oxidation of the dried residues from the tubes with fusion mixture.

α:β-(p:p-*Ditolyldimercapto*)-2:4-*dihydroxydiphenylmethane* (VII). —The residue (A) from the previous experiment was soluble only in pyridine, and was crystallised from a mixture of pyridine and alcohol in brick-red, micro-crystalline prisms. Yield about 40%. It decomposes at high temperatures and does not melt up to 300°. (Found: C, 72·5 ; H, 5·6 ; S, 14·7. $C_{27}H_{24}S_2O_2$ requires C, 72·9 ; H, 5·4; S, 14·4 per cent.).

The *potassium salt* was prepared as in the previous experiment. (Found: K, 14·8. $C_{27}H_{22}S_2O_2K_2$ requires K, 15·0 per cent.).

The *silver salt* was prepared from the potassium salt by adding silver nitrate solution till there was complete precipitation. It was warmed, filtered and washed throughly with hot water. (Found: Ag, 32·75. $C_{27}H_{22}S_2O_2Ag_2$ requires Ag, 32·85 per cent.).

Condensation of 2:4-*Dihydroxybenzhydrol with Phenyl Mercaptan.*—2:4-Dihydroxybenzhydrol (4 g.) was added as before to a mixture of concentrated sulphuric acid (25 c.c.) and phenyl mercaptan (3 g.) and the reaction carried out as in the previous experiment. After extraction with benzene and ether, the residue was crystallised from a mixture of ethyl acetate and alcohol in red micro-crystalline plates.

α-(*Phenylmercapto*)-2:4-*dihydroxydiphenylmethenesulphonic acid* (VIII), m.p. 191-195°, dissolves completely in alkali and alkali carbonate solutions. It is soluble in alcohol, acetone, chloroform and insoluble in inert solvents. (Found: C, 59·4 ; H, 3·9 ; S, 15·6. $C_{19}H_{16}S_2O_5$ requires C, 59·76; H, 4·12 ; S, 15·9 per cent.). In this condensation no disulphido-compound was obtained.

The *potassium salt* was obtained as in the previous cases. (Found: K, 23·3. $C_{19}H_{13}S_2O_5K_3$ requires K, 23·3 per cent.).

Condensation of 2:4-*Dihydroxybenzhydrol with Butylhydrosulphide.*—The product of the reaction between butyl hydrosulphide (6·6 g.), concentrated sulphuric acid (25 c.c.) and 2:4-dihydroxybenzhydrol (4·3 g.) was separated as in the case of the tolyl mercaptan derivatives. The residue insoluble in sodium carbonate was crystallised from alcohol in dark-brown prisms. This was the α:β-(*dibutyldithio*)-2:4-*dihydroxydiphenylmethane* (XI), m. p. 250° with decomposition. (Found: C, 66·34 ; H, 8·03 ; S, 17·3. $C_{21}H_{28}S_2O_2$ requires C, 66·12 ; H, 7·65 ; S, 17·02 per cent.).

The *potassium salt* was prepared by the usual method. (Found: K, 16·93. $C_{21}H_{26}S_2O_2K_2$ requires K, 17·25 per cent.). The alkaline filtrate from the dibutyl compound was neutralised

with dilute hydrochloric acid, when a dark-brown precipitate was obtained. α-(*Butylmercapto*)-2:4-*dihydroxydiphenylmethanesulphonic acid* (X) was crystallised from alcohol in dark-brown micro-crystalline plates, m. p. 146-147°. (Found: C, 55·1; H, 5·5. $C_{17}H_{20}S_2O_5$ requires C, 55·43; H, 5·4 per cent.).

The *potassium salt* was obtained as before. (Found: K, 24·51. $C_{17}H_{17}S_2O_5K_3$ requires K, 24·27 per cent.).

Condensation of 2:4-*Dihydroxybenzhydrol with Benzyl Mercaptan.*—The condensation was carried out as in the previous experiments. But on pouring into excess of ice-cold water, the solution turned dark brown in colour and no precipitate was deposited even when the solution was cooled in a freezing mixture. So it was treated with powdered calcium carbonate and the mixture was heated and the hot solution filtered. The filtrate, which contained the calcium salt of the sulphonic acid, was treated with sodium carbonate solution till the calcium carbonate was completely precipitated. It was filtered and the filtrate evaporated to dryness on a water-bath and then crystallised from a small quantity of water. From this potassium salt the free sulphonic acid was obtained by neutralising with concentrated hydrochloric acid and crystallised from alcohol in brown granular crystals. α-(*Benzylmercapto*)-2:4-*dihydroxydiphenylmethanesulphonic acid* has the m.p. 223-225°. Yield 50 %. It is completely soluble in alkali carbonate solutions.

The *potassium salt* prepared as before gave the following result. (Found: K, 22·41. $C_{20}H_{15}S_2O_5K_3$ repuires K, 22·24 per cent.).

Action of p-*Tolyl Mercaptan upon* (p-*Tolylmercapto*)-2:4-*dihydroxydiphenylmethanesulphonic Acid.*

Equimolecular quantities of the mercaptan and the sulphonic acid were condensed in the presence of concentrated sulphuric acid as in the previous experiments. The residue from sodium carbonate solution was crystallised from a mixture of pyridine and alcohol in brick-red micro-crystalline prisms, m.p. above 300°. This is identical with the ditolyl disulphido-compound (VII) originally obtained. Some unchanged sulphonic acid was recovered from the filtrate.

The *potassium* derivative of the disulphido-compound was prepared as before. (Found: K, 15·1. $C_{27}H_{22}S_2O_2K_2$ requires K, 15·0 per cent.).

Action of Butylhydrosulphide upon α-(*Phenylmercapto-*)-2:4-*dihydroxydiphenylmethanesulphonic Acid.*

Equimolecular quantities of the sulphonic acid (1 g.) and the mercaptan were placed in contact with concentrated sulphuric acid (5 c.c.), and the experiment was carried out as before. The product which was insoluble in hot sodium carbonate solution was washed well with hot water and crystallised from alcohol in deep brown micro-crystals. Yield 25-30%. (*α-Phenyl-β-butyl-dimercapto*)-2:4-*dihydroxydiphenylmethane* (XII) decomposes above 250°. (Found: C, 69·36 ; H, 6·51. $C_{23}H_{24}S_2O_2$ requires C, 69·6 ; H, 6·07 per cent.).

Action of p-*Tolyl Mercaptan upon α-(Phenylmercapto)*-2:4-*dihydroxydiphenylmethanesulphonic Acid.*

The condensation was carried out as in the previous experiments. The product thus obtained was purified by the usual method and isolated in a pure condition by crystallising from a mixture of pyridine and alcohol. Thus (*α-phenyl-β-p-tolyldimercapto*)-2:4-*dihydroxydiphenylmethane* (IX) was obtained in red micro-crystals. Yield 2[illegible]-30%. The compound decomposes at a high temperature.

Action of concentrated Sulphuric Acid upon αβ-(p: p-*Ditolyldimercapto*)-2:4-*dihydroxydiphenylmethane* (VII).

αβ-(Di-*p*-tolyldimercapto)-2:4-dihydroxydiphenylmethane (1 g.) was treated with 5 gm. of concentrated sulphuric acid and heated on a water-bath for 3 to 4 hours at a temperature of 40 to 60°. The next day it was poured into ice-cold water. Most of the substance went into solution except a small quantity of a red substance. This crude product melted at 148° but on crystallisation from alcohol it melted at 158-159° corresponding to *α*-(p-*tolylmercapto*)-2:4-*dihydroxydiphenylmethanesulphonic acid.* It was completely soluble in hot sodium carbonate solution. The mixed melting point also was 158-159°. The other decomposition products could not be isolated from the filtrate.

Condensation of 2:4-*Dihydroxy-4'-methoxybenzhydrol with* p-*Totyl Mercaptan.*—The mercaptan (3·6 g.), concentrated sulphuric acid (15 c.c.) and 2:4-dihydroxy-4'-methoxybenzhydrol (5·6 g.) were condensed together as before. The product, *α*-(p-*tolylmercapto*)-2:4-*dihydroxy-4'-methoxydiphenylmethanesulphonic acid* was crystallised from a mixture of ethyl acetate and alcohol or alcohol only in red micro-crystalline plates, m.p. 160-161°. It is completely soluble in hot sodium carbonate solution. It is sparingly soluble in alcohol, ethyl acetate, etc., insoluble in benzene, toluene etc., while greatly

soluble in acetone, chloroform and pyridine. (Found: C, 58·15 ; H, 4·80. $C_{21}H_{20}S_2O_6$ requires C, 58·33; H, 4·63 per cent.).

The *potassium* derivative was prepared as before. (Found: K, 21·73. $C_{21}H_{17}O_6S_2K_3$ requires K, 21·43 per cent.).

Condensation of 2:4-*Dihydroxy*-4'- *methoxybenzhydrol with Butyl Mercaptan.* - 2:4-Dihydroxy-4'-methoxybenzhydrol (1 mol.) and butylhydrosulphide (1½ mol.) were condensed as described in the previous experiment. On crystallisation from alcohol they gave deep brown micro-plates. α-(*Butylmercapto*-)- 2:4-*dihydroxy*-4'- *methoxydiphenylmethanesulphonic acid* decomposes at about 265°. It completely dissolves in hot sodium carbonate solution (Found: C, 58·73; H, 6·31. $C_{18}H_{22}S_2O_6$ requires C, 59·02; H, 6·02 per cent.).

The *potassium salt* gave the following result. (Found: K 22·51. $C_{18}H_{19}S_2O_6K_3$ requires K, 22·85 per cent.).

Condensation of Benzhydrol with Phenyl Mercaptan.—Thiophenol (4 g.) and benzhydrol (4 g.) were condensed as described in the previous experiments. The product was purified by ether and benzene, and finally extracted with a mixture of ethyl acetate and alcohol. The residue was crystallised from a mixture of pyridine and alcohol in colourless micro-prisms, m.p. 221-223°. This is α:β-(*diphenyldimercapto*)-*diphenylmethane*. It is insoluble in alkalis. In this case no sulphonic acid derivative could be isolated. (Found: S, 16·52. $C_{25}H_{20}S_2$ requires S, 16·7 per cent.).

Interaction of Benzhydrol with p-*Tolyl Mercaptan.*—The product of interaction between *p*-totyl mercaptan (5 g.), concentrated sulphuric acid (20 c.c.) and benzhydrol (4 g.) was extracted with 25% alcohol, in which a portion dissolved (A). The insoluble residue was then crystallised from a mixture of pyridine and alcohol in faintly reddish micro-prisms. This is α:β-(-p-*ditolyldimercapto*)-*diphenylmethane*, m.p. 251-252° with previous softening at 250°. (Found: S, 15·25. $C_{26}H_{24}S_2$ requires S, 15·53 per cent.).

α-(p-*Tolylmercapto*)-*diphenylmethanesulphonic Acid.*—The soluble portion (A) described in the previous experiment was obtained by evaporating off the alcohol and then purified by reprecipitating from the sodium salt by dilute hydrochloric acid solution. It was further purified by crystallisation from alcohol in colourless micro-plates, m.p. 163-164°. The yield was only 15%.(Found: S, 17·1. $C_{20}H_{18}S_2O_3$ requires S, 17·3 per cent.).

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Kinetics of the Catalytic Oxidation of Arsenious Acid with Ferric Chloride in Presence of Potassium Iodide.

By J. C. Sarma.

The reaction between ferric chloride and arsenious acid has been studied by Jellineck and Winogradoff (*Z. Elektrochem.*, 1924, **30**, 477). They found that the reaction is immeasurably slow at ordinary temperature and indeed a mixture of the two may be kept at ordinary temperature for months together without any apparent change. They, therefore, studied the reaction at two temperatures 107° and 127° by heating the reacting mixtures in sealed tubes and analysing the reaction products by a very laborious and round-about quantitative process in absence of any easy and exact volumetric method for determining the ferrous salt in the presence of arsenious acid. They found that under the conditions of the experiment, the order of the reaction is approximately trimolecular and reversible as follows:—

$$2FeCl_3 + H_3AsO_3 + H_2O \rightleftarrows 2FeCl_2 + H_3AsO_4 + 2HCl.$$

The present investigation was undertaken with a view, firstly, to find whether with the addition of a suitable catalyst, the reaction may be made to proceed with a measurable velocity at ordinary or any conveniently lower temperature, and secondly, to find out an easier volumetric method for following the reaction and studying the equilibrium conditions. Both of these were achieved after a few initial trials and experiments and the results obtained will be set out in the following pages.

It was observed that traces of potassium iodide strongly catalyse the reaction which proceeds with measurable velocity at ordinary temperatures (25°-30°) though the final equilibrium is attained very slowly at the end of days. The reaction was, therefore, more conveniently studied at 50° and 60° at which the final equilibrium is attained within 10 to 12 hours.

Next in our search for a suitable oxidising reagent for estimating volumetrically the ferrous salt in presence of both ferric salt and arsenious acid, it was found that ceric sulphate in sulphuric acid solution with diphenylamine hydrochloride as an internal indicator answers the purpose very well. Willard and Young (*J. Amer.*

Chem. Soc., 1928, **50**, 1335) have shown the use of ceric sulphate as an oxidising volumetric reagent and their method with some modifications was used for this purpose.

Outline of the Process.

The following solutions were used for the experiments—

(*a*) An approximately 0·320*N* solution of ferric chloride in 0·05 *N*-HCl solution.

(*b*) An almost saturated solution of solid arsenious acid in water, the strength of the solution being 0·3254*N* approximately at 30°.

(*c*) An *N*/100 solution of pure potassium iodide in water. Different quantities of which were used as catalyser.

(*d*) A dilute solution of ceric sulphate (approximately *N*/100) in *N*-sulphuric acid was used as the volumetric oxidising reagent.

(*e*) A solution of glacial phosphoric acid (*d* 1·7) in the proportion of 150 c.c. per litre.

(*f*) A dilute solution of diphenylamine hydrochloride in sulphuric acid in the proportion of 1 gm. of the amine salt in 100 c.c. of sulphuric acid (*d* 1·84). A drop or two of this solution was used as an internal indicator for finding the end-point in the titrations.

(*g*) A saturated solution of silver sulphate.

For equilibrium experiments, definite volumes of arsenious acid, ferric chloride, potassium iodide and hydrochloric acid solutions were mixed in glass bottles with ground-glass stoppers and kept in the thermostat, the temperature of which was maintained constant within ± 1°. After 10 to 12 hours, 5 c.c. of the equilibrium mixture were taken out and poured into 50 c.c. of ice-cold freshly boiled distilled water. 10 C.c. of saturated silver sulphate solution were added to precipitate the iodide completely. 5 C.c. of phosphoric acid were then added and two drops of the diphenylamine indicator. The end point is quite sharp and is indicated by the appearance of a persistent bluish-violet coloration with a drop of a *N*/100-ceric sulphate solution. For kinetic measurements the solutions of all the reacting substances were kept in glass stoppered bottles in the thermostat till they attained the temperature of the bath. Definite volumes of the solutions were then measured out into the reacting vessel and last of all 1 or 2 c.c. of potassium iodide solution, the catalyser, was added. The reaction was followed by taking out 5 c.c. of the mixture from time to time and titrating with ceric sulphate solution as described above. Air-free conductivity water was used in all these experiments.

Equilibrium Experiments.

TABLE I.

Temperature = 50°. Concentration of the catalyst = 0·0015*N*.

$$K = \frac{[H_3AsO_3] \times [FeCl_3]^2}{[H_3AsO_4] \times [FeCl_2]^2 \times [HCl]^2}.$$

Expt.	Initial concentration of the solution in gm. mol. per litre. H_3AsO_3.	$FeCl_3$.	HCl.	Equilibrium concentration of the solution in gm. mols. per litre. H_3AsO_3.	$FeCl_3$.	H_3AsO_4.	$FeCl_2$.	HCl.	*K*.
1.	$2·325 \times 10^{-2}$	$4·65 \times 10^{-2}$	0·340	$1·25 \times 10^{-2}$	$2·5 \times 10^{-2}$	$2·2 \times 10^{-2}$	$4·4 \times 11^{-2}$	0·384	$1·24 \times 10^{-3}$
2.	,,	,,	0·643	$1·75 \times 10^{-2}$	$3·5 \times 10^{-2}$	$2·15 \times 10^{-2}$	$4·3 \times 10^{-2}$	0·686	$1·30 \times 10^{-3}$
3.	,,	,,	1·243	$2·75 \times 10^{-2}$	$5·5 \times 10^{-2}$	$2·05 \times 10^{-2}$	$4·1 \times 10^{-2}$	1·284	$1·47 \times 10^{-3}$
4.	,,	,,	2·418	$4·15 \times 10^{-2}$	$8·3 \times 10^{-2}$	$1·91 \times 10^{-2}$	$3·82 \times 10^{-2}$	2·456	$1·70 \times 10^{-3}$
5.	,,	,,	3·607	$4·80 \times 10^{-2}$	$9·6 \times 10^{-2}$	$1·845 \times 10^{-2}$	$3·69 \times 10^{-2}$	3·644	$1·34 \times 10^{-3}$
6.	$3·755 \times 10^{-2}$	$1·2 \times 10^{-1}$	2·673	$1·05 \times 10^{-2}$	$4·7 \times 10^{-2}$	$3·65 \times 10^{-2}$	$7·30 \times 10^{-2}$	2·746	$1·58 \times 10^{-3}$
7.	,,	,,	3·582	$1·45 \times 10^{-2}$	$4·78 \times 10^{-2}$	$3·61 + 10^{-2}$	$7·22 \times 10^{-2}$	3·654	$1·32 \times 10^{-3}$
									Mean $1·42 \times 10^{-3}$

TABLE II.

Temperature = 60°.

1.	$2·325 \times 10^{-2}$	$4·65 \times 10^{-2}$	0·643	$2·25 \times 10^{-2}$	$4·5 \times 10^{-2}$	$2·1 \times 10^{-2}$	$4·2 \times 10^{-2}$	0·684	$2·60 \times 10^{-3}$
2.	,,	,,	2·418	$4·70 \times 10^{-2}$	$9·4 \times 10^{-2}$	$1·85 \times 10^{-2}$	$3·71 \times 10^{-2}$	2·452	$2·71 \times 10^{-3}$
3.	$3·755 \times 10^{-2}$	$1·2 \times 10^{-1}$	2·673	$1·70 \times 10^{-2}$	$4·83 \times 10^{-2}$	$3·585 \times 10^{-2}$	$7·17 \times 10^{-2}$	2·744	$2·85 \times 10^{-3}$
4.	,,	,,	3·582	$2·4 \times 10^{-2}$	$4·97 \times 10^{-2}$	$3·515 \times 10^{-2}$	$7·03 \times 10^{-2}$	3·652	$2·55 \times 10^{-3}$
									Mean 2·68 × 10

Heat of the reaction.—According to vant Hoff's equation for the reaction isochore, we have, $\frac{d \log K}{dT} = \frac{-Q}{RT^2}$ which on integration gives $\log_e K_1 - \log_e K_2 = \frac{Q}{R} \times \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$. Substituting the values of K_1 and K_2 for 60° and 50°, we have log 0·00268 − log 0·00142 = $\frac{Q}{4{\cdot}58}\left(\frac{1}{333} - \frac{1}{323}\right)$ or $Q = -13600$ calories.

This shows that the heat of the reaction is considerable and 13600 calories are evolved when 1 gm. mol. of arsenious acid is oxidised by 2 gm. mols. of ferric chloride with the formation of 1 gm. mol. of arsenic acid, 2 gm. mols. of ferrous chloride and 2 gm. mols. of hydrochloric acid. Jellineck and Winogradoff (*loc. cit.*) found this value to be about 18000 calories. But in view of the inaccurate and complicated methods they adopted in their analysis, we assume that our data are more accurate than theirs.

Kinetic Measurements.—The following measurements were done to determine the order of the reaction with respect to arsenious acid and ferric chloride separately.

TABLE III.

Temperature = 50°.

$FeCl_3 = 0{\cdot}03N$. $H_3AsO_3 = 0{\cdot}242N$. $HCl = 0{\cdot}02N$. $KI = 0{\cdot}0007N$.

Time in mins.	x.	$a-x$.	k (monomolecular).
0	0	0·030	—
7	0·0047	0·0253	0·88
14	0·0083	0·0217	0·91
24	0·0116	0·0184	0·87
34	0·0140	0·0160	0·86
54	0·0175	0·0125	0·86
122	0·0228	0·0072	0·90

TABLE IV.

Temperature = 50°.

$H_3AsO_3 = 0{\cdot}0488N$. $FeCl_3 = 0{\cdot}197N$. $HCl = 0{\cdot}05N$. $KI = 0{\cdot}0007N$.

Time in mins.	$a-x$.	$\log\frac{a}{a-x}$.	k (bimolecular).
0	0·0488	—	—
7	0·0328	0·1703	$5{\cdot}7\times10^{-3}$
14	0·0210	0·3660	$6{\cdot}0\times10^{-3}$
24	0·0120	0·5798	$5{\cdot}6\times10^{-3}$
34	0·0078	0·7965	$5{\cdot}4\times10^{-3}$
70	0·00137	1·5502	$5{\cdot}1\times10^{-3}$

It will appear evident that the reaction is bimolecular with respect to ferric chloride and monomolecular with respect to arsenious acid. The constants obtained in Tables III and IV are fairly good.

The following experiments were then carried out to see how far the equation for a trimolecular reaction holds good and also to observe the influence of different concentrations of the catalyst on the reaction velocity. For a trimolecular reaction, we have

$$k = \frac{1.\ x(2a-x)}{t.2a^2(a-x)^2}$$

TABLE V.

Concentration of all the reacting substances are taken in gm. equivalents per litre.

$H_3AsO_3 = 0{\cdot}0474N$. $FeCl_3 = 0{\cdot}0474N$. $HCl = 0{\cdot}015N$. $KI = 0{\cdot}003N$.

Temperature = 50°.

Time in mins.	x.	$2a-x$.	$(a-x)^2$.	k (trimolecular).
0	0	$9{\cdot}48\times10^{-2}$	$2{\cdot}25\times10^{-3}$	—
7	$1{\cdot}75\times10^{-2}$	$7{\cdot}75\times10^{-2}$	$9{\cdot}0\times10^{-4}$	47·98
14	$2{\cdot}33\times10^{-2}$	$7{\cdot}15\times10^{-2}$	$5{\cdot}58\times10^{-4}$	45·72
24	$2{\cdot}70\times10^{-2}$	$6{\cdot}78\times10^{-2}$	$4{\cdot}16\times10^{-4}$	40·83
54	$3{\cdot}24\times10^{-2}$	$6{\cdot}24\times10^{-2}$	$2{\cdot}25\times10^{-4}$	36·98

The effect of varying concentrations of the catalyst and also of hydrochloric acid was next studied. It was found that the velocity

of the reaction is not directly proportional to the concentration but to a higher power of the concentration of the catalyst. The concentrations of the catalyst in our experiments were varied from 0·003*N* to 0·00075*N* whereas the value of *k* fell from 49·98 to 9·27. It was found that the concentration of hydrochloric acid has not a marked effect on the velocity of the reaction which falls off by 30% only whereas the concentration of HCl increased from 0·63*N* to 3·52*N*. The temperature coefficient for 10° between 50° and 60° was found to be 1·9 approximately. It is also significant that the velocity constant falls off by about 25% (compare Table V) for which we have attempted to offer an explanation later on.

Discussion.

The velocity of oxidation of arsenious acid by ferric chloride in aqueous solution proceeds with negligibly small velocity at 50°. But if potassium iodide is added then the velocity increases enormously. It appears probable that this reaction is really made up of the following two consecutive reactions:—

$$2Fe^{\cdots} + 2I' \longrightarrow 2Fe^{\cdot\cdot} + I_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$I_2 + H_3AsO_3 + H_2O \longrightarrow 2HI + H_3AsO_4 \quad \ldots\ldots\ldots\ldots \quad (2)$$

A similar reaction has been studied by Price (*Z. physikal. Chem.*, 1898, **27**, 476) and Federlin (*ibid*, 1902, **41**, 565). It consists in the oxidation of phosphorus acid by potassium persulphate with hydriodic acid as catalyst. The velocities of the following reactions,

$$K_2S_2O_8 + 2HI = K_2SO_4 + H_2SO_4 + I_2$$

$$H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI,$$

have been studied separately and it has been shown conclusively that the velocity of the complete reaction can be calculated from the velocities of the two consecutive reactions.

In this particular case however the velocity of the first reaction *i.e.*, the oxidation of iodine ion by ferric ion has a fairly large value (Sasaki, *Mm. Coll. Sci. Kyoto Imp. Univ.*, 1922, **5**, 315). We would therefore expect that the observed velocity constant of the complete reaction is really the velocity of the second reaction, *i.e.*, the oxidation of arsenious acid by iodine. This reaction has been studied by Roebuck (*J. Phys. Chem.*, 1902, **6**, 365; 1905, **9**, 727) who finds the

velocity constant to be 0·185 at 0° and the coefficient for a temperature interval of 10° is 3·39. On this basis the velocity constant at 50° will be 61·42. This value is of the same order of magnitude as those recorded in this paper.

It now remains to account for our experimental observation that the complete reaction is bimolecular with respect to ferric ion and monomolecular with respect to arsenious acid. The reaction between a ferric salt and an iodide is really a reversible one

$$2\,Fe^{\cdots} + 2I' \rightleftharpoons 2\,Fe^{\cdot\cdot} + I_2$$

and if equilibrium is attained fairly quickly, the concentration of iodine is

$$[I_2] = K.\frac{[Fe^{\cdots}]^2[I']^2}{[Fe^{\cdot\cdot}]^2}$$

This equilibrium constant is very sensitive to the intensity of illumination, the quantity of free iodine in equilibrium rapidly diminishing as the intensity of illumination is increased (Sasaki, *loc. cit.*; Rideal and Williams, *J. Chem. Soc.*, 1925, **127**, 416; Kistiakowsky, *J. Amer. Chem. Soc.*, 1927, **49**, 976). We may assume that in diffused sunlight in which the experiments were carried out, the concentration of I-ion is not far different from the concentration of potassium iodide added to the solution. Hence the concentration of free iodine is proportional to the square of the concentration of the ferric salt and inversely proportional to the square of the concentration of the ferrous salt.

At the beginning of the experiment the velocity of the second reaction will be proportional to the square of the concentration of ferric salt and to the concentration of arsenious acid. This has been actually found to be the case. But with the progress of the reaction as the concentration of ferrous ion increases, the equilibrium concentration of iodine will diminish and the trimolecular velocity constant will diminish in magnitude. This has also been found to be the case.

In conclusion, I should express my deep gratitude to Professor J. C. Ghosh at whose suggestion this investigation was undertaken and who took a keen interest during the progress of the work.

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Some Aspects of Biochemical Synthesis.*

By P. C. Mitter.

I wish to offer you my heartfelt thanks for the great honour you have done me by asking me to preside over the deliberations of this section and though fully aware of my own limitations, I venture to hope that with your good will and co-operation we may bring the session to a successful issue.

Before beginning my address, I wish to refer to the great loss which our science has sufferred by the death of Prof. W. H. Perkin (jun.). Following in the footsteps of his illustrious father, Prof. Perkin incorporated in himself the highest and the best in the English School of Chemistry and the void which he has left will be difficult to fill.

I have chosen, as the subject of my address, " Some Aspects of Biochemical Synthesis."

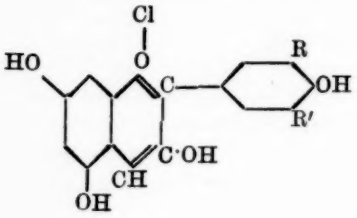
Although a little over a hundred years have elapsed since Wöhler by his synthesis of urea demonstrated that vital products could be synthesised in the laboratory, the mechanism of the formation of these products is still shrouded in mystery. The small temperature and pressure range between which they are formed and the absence of the usual reagents heighten the mystery still further. Very little is known for instance about the formation of the starches, celluloses and the proteins, not to speak of the living protoplasm, which is one of the most important factors in biochemical synthesis.

The vital products might be compared to links in a long chain, of which only the end members are visible and probably also a little of the beginning. But there are frequent indications in the products themselves or in the substances with which they are associated, which give some clue as to their modes of formation in nature.

On *a priori* grounds, we may expect certain similarity between different classes of natural products, certain uniformity of design depending on similarity in the modes of their formation and as a matter of fact a

* Presidential address to the Chemistry Section of the Seventeenth Indian Science Congress, held on 6th January, 1930 at Allahabad.

close examination often reveals many points of resemblance between diverse classes of vital products. In products of the same class again certain distinct sub-classes are often met with. Thus, the researches of Willstätter and his pupils[1] have shown that the anthocyanins are derived from the three prototypes pelargonidine, cyanidine and delphinidine



Pelargonidine: R=H, R′=H.
Cyanidine : R=H, R′=OH.
Delphinidine: R=OH, R′=OH.

all of which contain in the position 4′ of the phenyl radicle a free hydroxyl group. The hydroxyl group in the position 3 is linked with a sugar to from the anthocyanidin while the other hydroxyl groups are either free or blocked by methyl groups or form depside linkages with acids.

Similarly for the naturally occurring anthraquinone derivatives found among plant products, the following empirical laws have been found to hold good[2].

(1) No naturally occurring anthraquinone derivative contains more than four substituent groups in the two benzene nuclei, namely, not more than *one* methyl (or carboxyl or carbinol group) which, if present, always occupies a β-position and not more than *three* hydroxyl groups.

(2) The substances containing the maximum number of substituents form the fundamental types and the other anthraquinone derivatives occurring in the same plant are all derived from this fundamental type, being either oxidation or reduction or etherification, etc., products of the same. The fundamental types are therefore also derivable by superposing the formulae of associated anthraquinones.

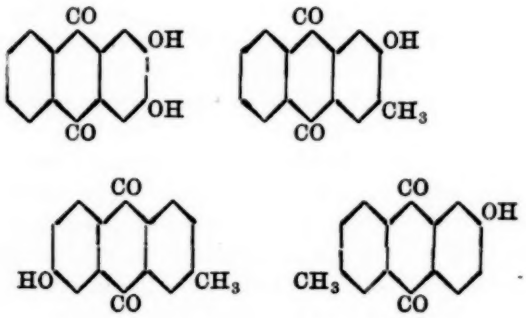
(3) Of the four substituents two (including the methyl or carboxyl or carbinol group, if present) occupy β-positions and the other two occupy α-positions.

(4) If both the β-substituents are in one ring the other groups also occur in the same ring or in other words, a homonuclear type is formed. If both the β-substituents are OH groups they must occur in the same ring.

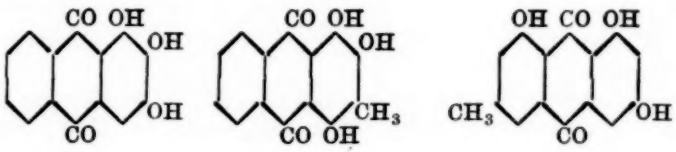
(5) If the β-substituents are in different rings the α-substituents are distributed in such a way as to produce a symmetrical configuration.

As no two types have three groups in common, it is possible by examining any one naturally occurring anthraquinone containing three substituents (sometimes even two substituents) to determine the fundamental type from which this particular substance and *all the other anthraquinone derivatives associated with it* have been derived.

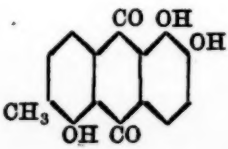
Starting from anthraquinone we get, by substituting two β-positions by two hydroxyl groups or by one hydroxyl and one methyl group, the following types :—



From these four β-substituted products we can derive the four fundamental types of naturally occurring anthraquinones—two homonuclear and two heteronuclear.



(I) (II) (III)



(IV)

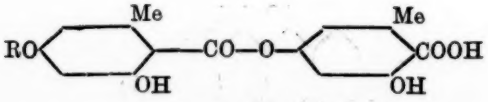
Any theory of the formation of anthraquinone derivatives in nature must therefore explain not only the formation of the anthraquinone ring system but in such a scheme the hydroxyl and methyl groups (if any) must occur in their proper places in the ring system. So it is obvious that a theory on the basis of which we arrive at a substituted anthraquinone derivative containing a configuration of groups unlike any present in nature, cannot be regarded as a correct approximation to truth. The polyketide hypothesis of Collie [3] suffers from this obvious drawback, although it offers a satisfactory explanation of the formation of the anthocyanine, cyanidine.

The task of the organic chemist, never an easy one, becomes particularly difficult in the case of those natural products which are not available in large quantities. The recognition of the fact, however, that nature seems to favour certain definite configuration of groups to the exclusion of others has often rendered an indirect method of determination of constitutions by previous synthesis and subsequent comparison and verification, possible.

The whole mass of internal evidence is in favour not of long chains owing their origin to cellulose material but of smaller units derived partly from this source, partly from the fragments of the protein molecules and partly from formaldehyde and its condensation products. Only with such small building units is it possible to explain the great diversity of types found among vital products.

The most satisfactory explanation of the formation of an anthraquinone ring system, for instance, appears to be by the fusion of a phenolic nucleus with a benzaldehyde or benzoic acid or a second phenolic or phenolic acid nucleus and formaldehyde followed by subsequent oxidation. We are strengthened in this supposition by the fact that there are numerous other vital products in which phenolic nuclei occur and these may, therefore, be regarded as among the fundamental building units.

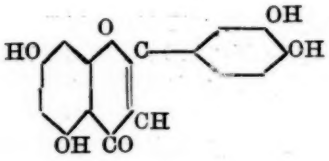
Among lichen acids, we have substances like lecanoric acid and evernic acid consisting of two phenolic acid nuclei united together by the so-called depside linkage,



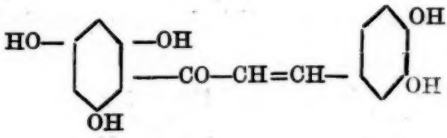
Lecanoric acid (R=H) ; Evernic acid (R=Me)

and some of the tannins contains such depsides linked with sugar molecules. Many of the anthocyanines again contain, besides the colouring matter proper with its phloroglucin component and the sugar radicles, a phenolic acid as a third constituent. As for instance, delphinine contains *p*-oxybenzoic acid and monardeine, *p*-oxycinnamic acid and this phenomenon according to Karrer[4] establishes a relation between the anthocyanines and the depsides and tannins with which they are often associated in the plant.

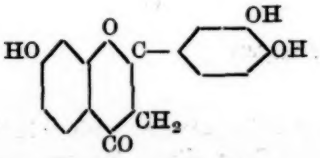
Among the vital products there are numerous ketones, some like paeonol or fisetol being fat-aromatic, others like the oxybenzophenones being diaryl ketones. The first of these two classes of ketones forms the transition to chalkones, flavones, flavonols and anthocyanines and finally to the epicatechins, and Freudenberg[5] has shown that these are all inter-related being members of an oxidation series.



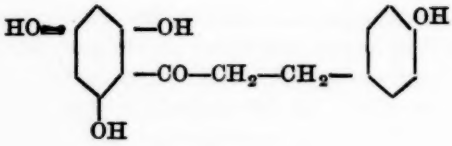
Flavone : Luteolin.



Eriodictyol : Chalkone.



Flavanone : Butin.

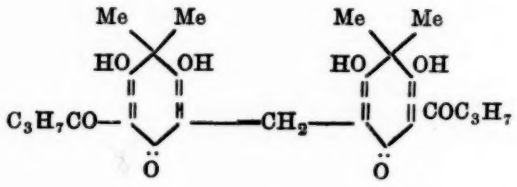


Phloretin.

Closely allied to the flavones are the *iso*flavones like genistein[6] which may be regarded as composed of a phenyl acetic acid nucleus, a phloroglucin nucleus and a formyl group. The first is also fairly well-distributed in nature and Gadamer[7] has shown that the alkaloids of the Chelidonium group may be regarded as derived from *N*-methyl phenylethylamine with formaldehyde and phenylacetaldehyde, the phenylacetaldehyde and phenyl ethylamine being derived from phenylalanine:

$$C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot COOH \rightarrow C_6H_5\cdot CH_2\cdot CH(OH)\cdot COOH$$
$$\rightarrow C_6H_5CH_2\cdot CHO + H\cdot COOH \text{(Ehrlich)}$$
$$C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot COOH \rightarrow C_6H_5\cdot CH_2\cdot CO\cdot COOH \rightarrow C_6H_5\cdot CH_2\cdot CHO$$
$$+CO_2 \text{(Neubauer)}$$
$$C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot COOH \rightarrow C_6H_5\cdot CH_2\cdot CH_2NH_2 \quad \text{(Ellinger)}$$

There are other types in which two phenolic nuclei are united by a $-CH_2-$ group or by a ketonic group. An example of the first type is the lichen-product albaspidin investigated by Boehm[8] which may be regarded as built up of phloroglucin, formaldehyde and butyraldehyde.[8a]



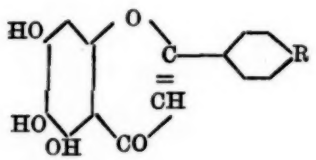
Albaspidin.

The hydroxylated diaryl ketones either occur as such or in the form of their anhydrides, the xanthones. From diaryl ketones there is a a transition over 3-oxy-4-phenylchromanes to brazilin and haematoxylin

and it is curious to note that the carbinol group in brazilin and haemotoxylin occupies the same position in the pyrone ring as the carbinol group in flavonols,[9] anthocyanines and even in catechin.[9a] In the laboratory a flavonol can be synthesised from a dihydric or trihydric phenol like resorcinol, or phloroglucinol, methoxyacetic acid and an aromatic acid [10] and these are probably also the building units in the vital synthesis of flavonols. We should not be far wrong if we were to attribute to the carbinol group in flavonols, anthocyanidins, catechins and also perhaps in brazilin and haematoxylin, a common origin from a glycollic acid residue.

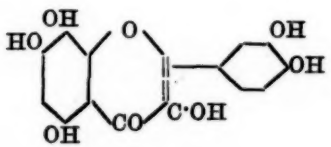
Among the phenol derivatives occurring among plant products, phloroglucin is easily the most widely distributed. The phloroglucin residue is found in oxybenzophenones like maclurin, xanthones (like gentisin) and it is fused with the γ-pyrone ring in most of the flavones and flavonols (even in an *iso*flavone like genistein,)[11] in all the anthocyanines and also in catechin.

In a few cases, a resorcin residue is linked with the γ-pyrone ring, as for instance in fisetin and in the flavanone butin, while a tetrahydric phenol (oxidation product of phloroglucin) nucleus occurs in the flavones scutellarein [12] and baikalein [13],



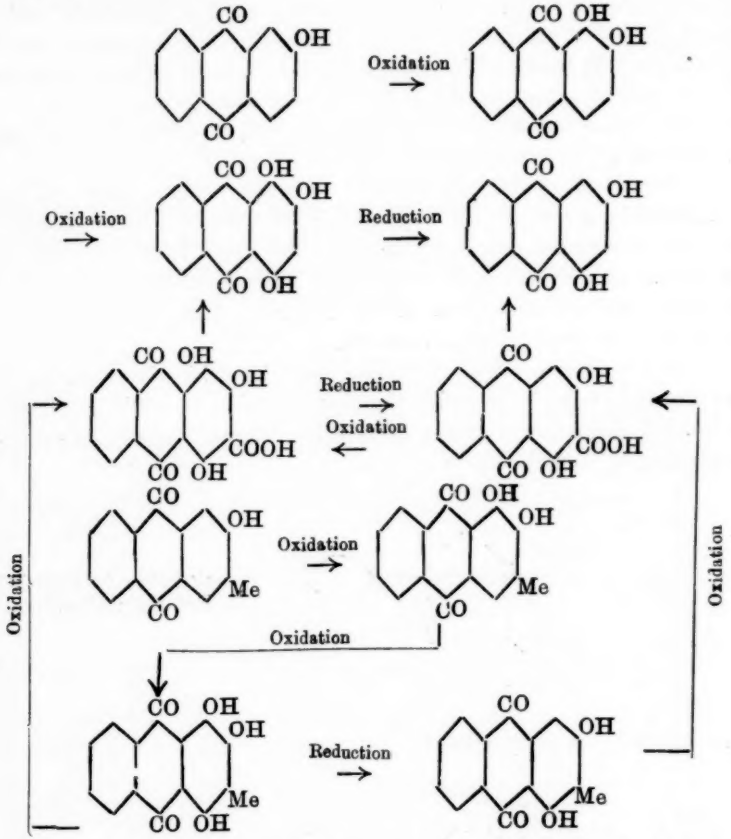
Scutellarein (R=OH)
Baikalein (R=H)

and the flavonol gossypetin [14].

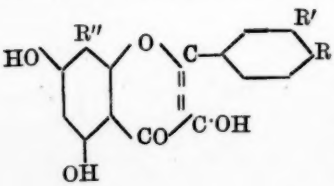


The second benzene nucleus in all the compounds mentioned above offers more variety and we have not only unsubstituted benzene nuclei (*e.g.* chrysin) but also hydroxyl groups in the position 2′ (datiscetin) [15], 4′ (apigenin), 2′:4′ (lotoflavin), 3′:4′ (quercetin) and 3′:4′:5′ (myricetin).

Oxidation and reduction chains are very common in nature and it has been found for instance that all the anthraquinones of the chayroot and madder types can be arranged in the form of such oxidation and reduction chains.[16]



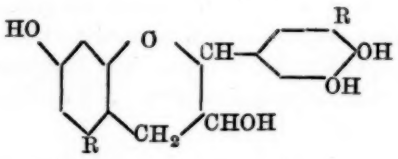
Among the flavones, flavonols and tannins also we meet with substances so related, occurring together



Quercetin, R=OH, R′=OH, R″=H;
Kaempherol, R=OH, R′=H, R″=H;
Kaempherid, R=OCH_3, R′=H, R″=H;
Galangin, R=H, R′=H, R″=H;
Gossypetin, R=OH, R′=OH, R″=OH.

as for instance quercetin and kaemferol, kaemferid and galangin, scutellarein and baikalein, gossypetin and quercetin, and quercetin with catechin and epicatechin. The simultaneous presence of gossypetin [17] and quercetin in *Hibiscus sabdariffa* furnishes the necessary connecting link between phloroglucin and 1:2:3:5-tetraoxybenzene.

The observed close association in nature of allied substances in different stages of oxidation has often afforded valuable clues to the constitution of unknown substances. Thus from the fact that quercetin and catechin occur together, A. G. Perkin and Joshitake [18] had inferred a formula for catechin which was verified by Freudenberg [19] and his co-workers later on. From the fact that quebrachotannin is accompanied by fisetin and pistachiotannin by myricetin, they have predicted the formulas of some of the hypothetical catechins which are the mother substances of tannins.



Quebrachocatechin, R=H.

Pistachiocatechin, R=OH.

We see also that phloroglucin is one of the fundamental building units in vital synthesis forming, as it were, the keystone in the architecture of diverse classes of compound. Its progressive reduction would give resorcin and phenol and finally benzene and from phenol again by oxidation catechol and hydroquinone may be obtained. It is well-known that phenol may be oxidised by hydrogen peroxide to catechol and the simultaneous presence of substances, containing one a phenol and the other a catechol nucleus or one a phenol and another a benzene nucleus, point to a common origin for corresponding portions of the molecules.* The ease with which phloroglucin may be methylated in the ring accounts for the presence of the methylphloroglucin skeleton and its reduction product, the methylresorcin skeleton which is found in rubiadin and (in its oxidised form) in euxanthone and probably also in munjisthin.

* An example of peculiar biochemical interest is furnished by the pair, scutellarein baikalein, the former containing a phenolic nucleus being found in the leaves, while the latter containing an unsubstituted benzene ring occurs in the roots.

As regards phloroglucin, we can trace its origin to sugar which is the first product of carbon dioxide assimilation by the green plant. The bridge to the cyclic compounds is formed most probably by inositol which is very largely distributed in nature and which can be connected with phloroglucin by a simple relation:—

$$C_6H_6(OH)_6 = C_6H_3(OH)_3 + 3H_2O.$$

Inositol Phloroglucin

The formation of a hydroaromatic compound from an aliphatic sugar has not been hitherto observed, nor the conversion of inositol to carbohydrates. The evidence of the relation between inositol and sugar is of an indirect character. Neuberg [20] has observed that by carefully heating inositol with phosphorus pentoxide, furfurol, which has always been regarded as a true carbohydrate derivative, is obtained. Besides, the cycloses serve on the one hand as reserve material for the living organism and are on the other hand converted by bacterial action to open-chain compounds like propionic, butyric and lactic acids, thereby disclosing their biochemical relationship with the carbohydrates.[21]

As regards the pyrogallol nucleus, it may be regarded as derived from 1:2:3:5-tetraoxybenzene by reduction. It is not without interest that the root bark of *Fagara xanthoxyloides* Lam. *Rutacae* contains the substances bergapten and xanthotoxin,[22] which have a common oxidation product.

Another fundamental unit in the formation of vital products is the isoprene unit. A critical examination by Ruzicka [23] has shown that the skeletons of members of the terpene family are formed by the regular union of isoprene units in a majority of cases and irregular in others. By regular union, Ruzicka means the union of isoprene units end to end, unlike ends being joined together and it must be conceded that the majority of terpenes possess such skeletal arrangements.

Myrcene and ocimene are both formed by the union of two isoprene units in such a way that the end carbon atom of the shortest chain of one unit, is attached to the end carbon atom of the longest chain of the other, the point of reference being the tertiary carbon atom.

TABLE I.

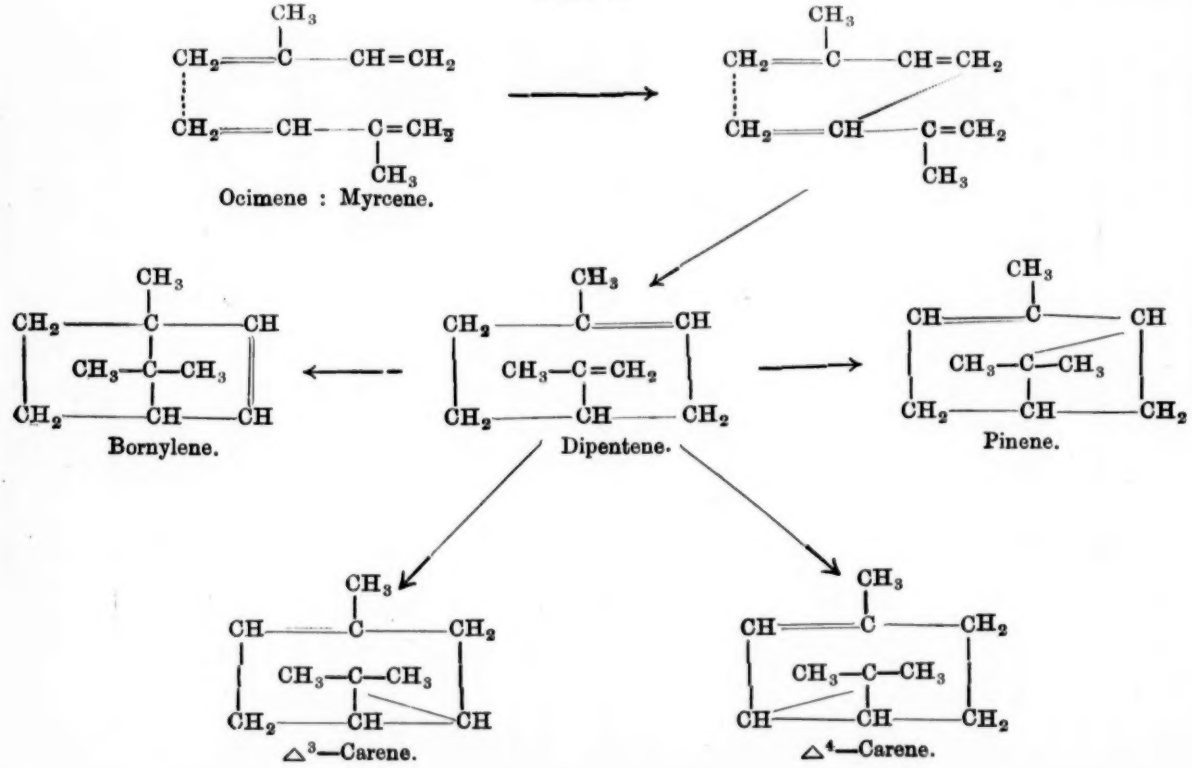
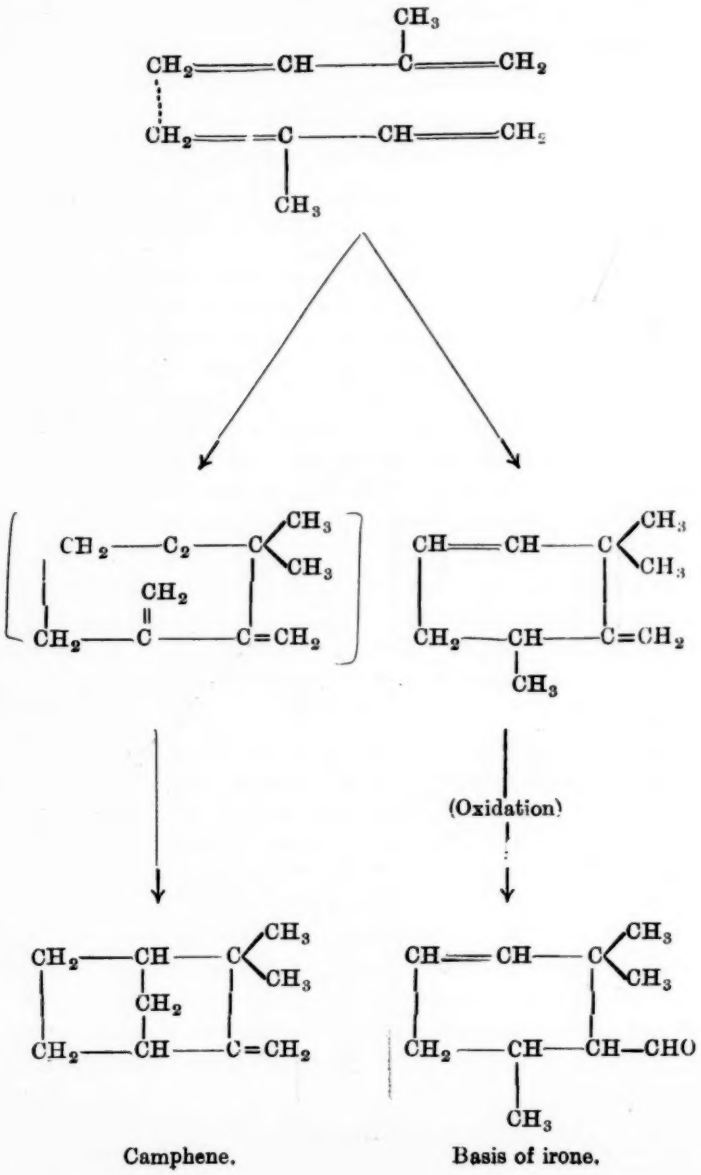
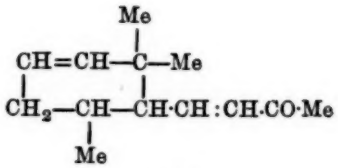

Ocimene : Myrcene.
Bornylene.
Dipentene.
Pinene.
△3—Carene.
△4—Carene.

TABLE II.



Camphene. Basis of irone.

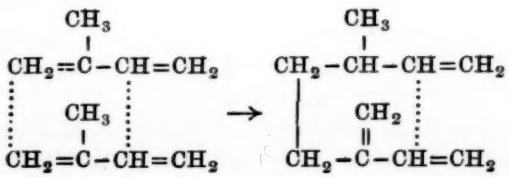
They form the transition on the one hand to the monocyclic terpenes of the *p*-cymene series, subsequent ring closing taking place in such a way as to leave the *iso*propyl group outside the ring, giving rise to dipentene. Dipentene forms the transition to the bicyclic terpenes of the *p*-cymene series, pinene, $\triangle^3$-carene and $\triangle^4$-carene. Other modes of closing of the primary ring are also possible. In the first of these we have the type camphene which also forms a transition to the sesquiterpene α-santalene. It is interesting to note that cyclocitral may be regarded as formed by oxidation of the primary product and if we concede that the isoprene-skeleton is derived by the union of acetone with acetaldehyde, (both of them derivable from sugar) somewhat on the lines of one [24] of the methods of synthesis of the substance, we have the rather interesting fact

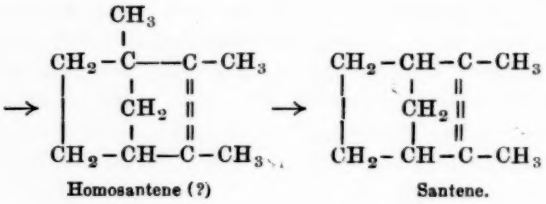


Irone.

of the irone skeleton being formed by the union of three acetone skeletons alternating with two acetaldehyde units.

As already stated before, the union of isoprene units to form the terpene skeletons is not restricted to regular union, that is to say union by unlike ends but there are cases where the union is irregular, *i.e.* union by like ends. If we denote the branched end of the isoprene nucleus by A and the other end by B, an union of the A−B−A−B type or of the B−A−B−A type would, according to Ruzicka, be regular while an union of the B−A−A−B or A−B−B−A type would be irregular. We find however that there are in nature instances of both types of union, although the former type predominates. Of instances of the latter we have sylvestrene where the union is of the A−B−B−A type and a compound of the B−A−A−B type is homosantene (hypothetical) whose lower homologue santene is known.





Homosantene (?) Santene.

In the case of sesquiterpenes again we know the constitution of compounds formed on the A–B–A–B–A–B model like cadenene, eudesmol, etc., but compounds formed on the B–A–A–B–B—A model are probably not absent when we find a similar constitution in substances like santonine. Judging from analogy, we can expect to find among compounds formed by the union of four isoprene units representatives of the type A–B–A–B–A–B–A–B and B–A–B–A–B–A–B–A as well as of the types A–B–B–A–A–B—B–A and B–A–A–B—B–A—A–B, and abietic acid which according to Ruzicka is formed by an " irregular " union of isoprene units [25] will be probably found to belong to one of the latter categories. Rao and Simonsen[26] have thrown some doubts on the occurrence of sylvestrene in nature and referred among others to the " anomalous " position which sylvestrene occupies being " the only naturally occurring terpene derived from *m*-cymene, all the other members of the group being *p*-cymene derivatives."

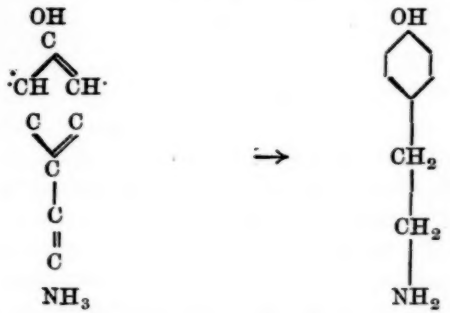
We have seen already that the " anomaly ", if any, is shared by at least two other natural products santene and santonine, the first of which is a terpene.

The absence of the characteristic colour reaction of sylvestrene in the oil from *Pinus sylvestris* need not surprise us when we consider that there are other substances in the mixture which also give colour reactions and the presence of which might disguise or inhibit the colour reaction due to pure sylvestrene. A curious error which might have influenced the views of the authors occurs in this paper. They observe: " It is not without significance that Atterberg[26a] in one experiment could obtain only a dihydrochloride, m.p. 50°(the melting point of dipentene dihydrochloride) since it has been shown that in some cases $\triangle^4$-carene on treatment with hydrogen chloride yields dipentene dihydrochloride in larger quantity than sylvestrene dihydrochloride and the former therefore crystallises on cooling. What Atterberg says however is this:—

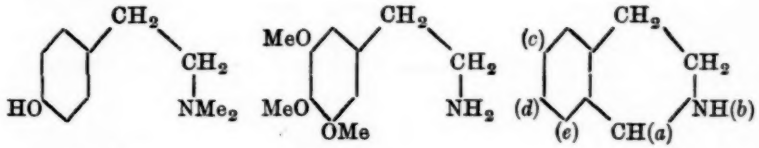
" Wie aus dem Obigen hervorgeht, ist das Sylvestren in Bezug zu den anderen bekannten Terpenen gut charakterisirt. Wie die anderen um

174° siedenden Terpene giebt es leicht ein Dichlorhydrat; dieses Chlorhydrat aber zeigt den Schmelzpunkt 72°-73° *während die anderen dargestellten Dichlorhydrate nicht höher als bei* 50° *schmelzen.*"

The isoprene skeleton is also met with in other natural products as for instance in the sugar, apiose $(CH_2OH)_2 : C(OH)\cdot CH(OH)\cdot CHO$. The alkaloid galegin $CMe_2 : CH\cdot CH_2\cdot NH\cdot C(:NH)\cdot NH_2$ furnishes an instance[27] in which an -NH- group is linked with the unbranched end of the isoprene nucleus. From a morphological point of view, it is difficult to resist the temptation of considering substances like *p*-oxy-*β*-phenylethylamine as being formed by the union of an isoprene unit with ammonia and a triose.



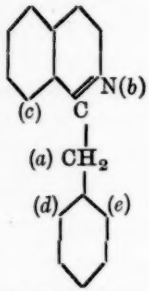
As regards the formation of alkaloids in nature we are on firmer grounds. "In any plant species in which a number of alkaloids occur it is almost invariably the case that they are closely related and can be regarded as marking stages in development." Thus the researches of Späth and his co-workers have shown that the *anhalonium* alkaloids are all closely related[27a].



Hordenine. Mezcaline.

Anhalamine: *a*=H, *b*=H, *c*, *d* and *e*=OH, OMe, OMe.
Anhalonidine *O*-methyl ether: *a*=Me, *b*=H, *c*, *d* and *e*=OMe.
Pellotine *O*-methyl ether: *a*=Me, *b*=Me, *c*, *d* and *e*=OMe.
Anhalonine: *a*=Me, *b*=H, *c*=OMe, *d* and *e*=.O.CH_2.O.
Lopophorine: *a*=Me, *b*=Me, *c*=OMe, *d* and *e*=.O.CH_2.O.

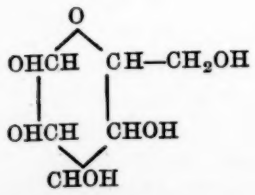
The alkaloids of the *iso*quinoline series like papaverine, narcotine, *iso*thebaine, berberine, etc., possess in common a benzyl *iso*quinoline nucleus. The same primary structure, gives by the insertion of a lactone ring between *a* and *d* the skeleton present in narcotine, while the formation of a link from *c* to *d* gives the nuclear structure present in *iso*thebaine and potentially present in morphine, codeine and thebaine. The insertion of a $-CH_2-$bridge between *b* and *e* gives the nucleus present in berberine, while a $-CHMe-$ bridge gives the nucleus of the corydaline subgroup. From the former by a further step the characteristic central structure of the alkaloids protopine and cryptopine can be derived.



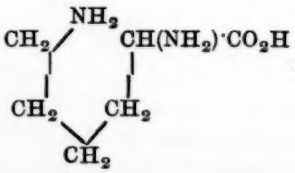
Robinson [28] has elaborated a scheme which suggests reactions by which the alkaloids might have been synthesised in plants. It involves in addition to the ordinary processes of methylation, methylenation, reduction, oxidation and dehydration, two types of condensation to provide for the linking up of carbon to carbon, namely the aldol condensation and the condensation of carbinol-amines containing the group $=C(OH)-N=$ with substances containing the group $=CH-CO-$.

The building units for the formation of alkaloids according to Robinson's scheme are the amines and amino-acids derived from the hydrolysis of proteins.

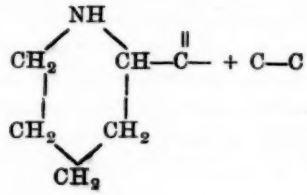
Haworth[29] has drawn attention to the intimate connection that appears to exist between the skeletal structure of the sugars and some of the amino-acids. "It is very probable", writes Haworth, "that there exists a direct relationship between the carbohydrates and the proteins and it appears clear according to the following analogies that these two groups, the most important of organic derivatives, possess a common origin.



Glucopyranose.



Lysine.



The connection of glucose with coniine, pelletierine, ψ-pelletierine and *iso*pelletierine in which the lateral chain of glucose is probably condensed with acetaldehyde or with a triose is an example. Similarly in the case of the alkaloids of the pyrrol group like stachydrin, betonicine etc. the lateral side chain of xylose is apparent.

There are other types of biochemical transformation of glucose, as for instance its conversion to a pyrone derivative kojic acid by the action of *Aspergillus oryzae*[30]. Besides, one of the products obtained by heating malt is α-methyl-β-hydroxy-γ-pyrone, maltol.

We see, therefore, that the units with which Nature synthesises her products are largely derived from the sugars or from the proteins at least some of which in their turn are derivable from the sugars, specially the hexoses and pentoses and it is easy to understand that there would be a tendency to exaggerate their importance. For instance, the methyl pentoses, which are fairly well represented in nature have been regarded as being formed not as primary products of biochemical synthesis but as secondary products derived from the hexoses by the reduction[31] of the terminal $-CH_2OH$ group to a $-CH_3$ group. Votoček[32] has pointed difficulties attendant on such a point of view. If the pentoses were formed from the corresponding hexoses, by a reduction process of this type, *iso*rhodeose which corresponds to glucose would have been one of the commonest of methyl pentoses. On the other hand, fucose which is actually so largely distributed in nature would have been rare, since the hexose from which it is derivable by reduction namely *l*-galactose is extremely rare in the vegetable kingdom. To obviate these difficulties Votoček suggests that we should seek the source of the methyl pentoses in the condensation of aldehydes containing methyl groups like acetaldehyde or perhaps lactic aldehyde with formic or glycollic or glyceric aldehyde.

In a recent communication, Robinson[33] has further elaborated a scheme indicating the relationship of some complex natural products to the sugars and amino-acids and pointed out *inter alia* that the ornithine skeleton is also present in histidine, the lysine in quinine while nicotine

contains both ornithine and lysine skeletons. Harmaline and physostigmine can both be derived from the amino-acid tryptophane, while in chlorophyll and haemin the sugar skeletons are perceptible.

We see, therefore, that the conditions prevailing in nature favour the formation of certain distinct classes of compounds, having common frameworks and that there are sub-classes within these classes, which differ from one another in the number and disposition of substituent groups.

The vital products belonging to different classes are sometimes related in such a way as to mark stages in development; and when, as is often the case, such substances occur together, they offer valuable clues as to the course of the biochemical synthesis.

The building units in vital synthesis are derived partly from formaldehyde and its condensation or alteration products, chiefly the sugars and partly from the amino-acids (some of which are themselves derivable from the sugars) which are the products of protein hydrolysis, "the molecular *debris*, strewing the path of enzyme action."

The whole mass of internal evidence is in favour of comparatively small building units, without assuming which it is difficult to explain the great variety of types that are met with in nature.

Diverse products are formed in the living organism, some as the result of the anabolic, others again of the catabolic processes taking place in it and these again suffer various secondary changes like oxidation, reduction methylation, methylenation, hydrolysis and aldol and carbinolamine condensations giving rise to the various kaleidoscopic patterns with which nature greets our eyes or delights our senses.

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Velocity of Reaction in Mixed Solvents. Part I. The Velocity of Reaction between Potassium Persulphate and Potassium Iodide in Organic Solvents-Water Mixtures.

By Mata Prasad, C. L. Mankodi and R. D. Godbole.

Velocities of several chemical reactions in various solvents and mixtures of solvents have been found to be either accelerated or retarded. Cohen (*Z. physikal. Chem.*, 1899, **38**, 145) found that the hydrolysis of cane-sugar was retarded by the addition of alcohol to water. On the other hand, Walker and Kay (*J. Chem. Soc.*, 1897, **71**, 480) found that the transformation of ammonium cyanate to carbamide in water was greatly accelerated by the addition of alcohol. Also Patterson and Forsyth (*J. Chem. Soc.*, 1912, **101**, 40) found that methyl alcohol and acetone accelerated the reaction between iodic and sulphurous acids.

Bhonson (*J. Phys. Chem.*, 1920, **24**, 677) studied the catalytic decomposition of hydrogen peroxide in mixed solvents and found that solvents exerted a specific effect on the velocity of reaction. Gosta Akerlof (*J. Amer. Chem. Soc.*, 1928, **50**, 1272) studied the decomposition of diacetone alcohol by sodium hydroxide, in water mixtures of organic solvents and found that in some of the pure alcohols the reaction velocity was largely influenced by traces of water, this influence decreasing with decreasing molocular weight of the alcohol or with increasing number of hydroxyl groups.

In view of the additive properties of mixtures, it is expected that the velocity of a reaction in mixed solvents will be intermediate between those in pure solvents and that the velocity constant—composition curves will be straight lines. Millar and Braune (*J. Chem. Soc.*, 1913, **85**, 1701) studied the decomposition of diazoacetic ester in alcohol—water mixtures and found a minimum in the

velocity constant-composition curve at 11 per cent. of water. Cashmore, McCombie, Scarborough and others (*J. Chem. Soc.*, 1921, **119**, 970; 1922, **121**, 2421, 2301, 1229; 1923, **123**, 2688,) studied the esterification of a number of esters in water-alcoholic mixtures and pointed out that the breaks in the velocity constant—composition curves occurred at such compositions of the solvents which in most cases are those demanded by simple complexes of alcohol and water.

In the present investigation the reaction between potassium persulphate and potassium iodide has been studied in mixtures of organic solvents and water. In aqueous solutions the kinetics of the reaction, which takes place as $K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$, was first studied by Price (*Z. physikal. Chem.*, 1898, **27**, 474) who using different methods for determining the order of a reaction, found the reaction to be of the second order. But Price had noticed that there was a slight divergence in experimental results calculated from the second order formula and these differences increased with the time for which the reaction was studied.

Experimental.

The velocity of the reaction has been studied in mixtures of water with methyl, ethyl and propyl alcohols, glycol, glycerol and pyridine.

Extra pure (Kahlbaum's) potassium persulphate was purified by crystallisation several times. The purity of the sample was determined by titrating the crystallised salt with ferrous sulphate. As potassium persulphate decomposes when exposed to light, it was kept in bottles wrapped in black paper.

Potassium iodide used was Merck's extra pure chemical and was found to be free from iodate.

All the organic solvents used were Merck's extra pure chemicals and were purified by the usual methods of dehydration and distillation.

Solutions of potassium persulphate and potassium iodide were made in water, redistilled from alkaline permanganate, fresh every time a reading was taken. The desired quantity of the organic solvents was added to one of the solutions and the two solutions were

placed in a thermostat maintained at 25°. When they had acquired the temperature of the bath, they were mixed and it was so arranged in all the experiments that the initial concentrations of potassium iodide and potassium persulphate in the mixture were $N/50$. The total volume of the reaction mixure was 100 c.c. but in experiments where higher percentages of the organic solvents were used, it was increased to 250 c. c.

Potassium persulphate is a great oxidising agent and consequently low concentrations of potassium persulphate were used to avoid or to minimise the oxidation of alcohols. Also the error caused by the interaction of the liberated iodine with the organic solvents would be very insignificant as the velocity of the above reaction is extremly slow. Ten or 25 c. c. of the reaction mixture were removed to conical flasks, containing ice-cold water, at difierent intervals and the amount of the liberated iodine was determined by titrating the mixture against $N/100$-sodium thiosulphate solution. The reaction was usually allowed to proceed for two to three hours but in mixtures containing higher percentage of the organic solvents, it was continued for a longer time.

In calculating the results the initial concentration, a, of potassium iodide and persulphate and the amount of the liberated iodine, x, are expressed in terms of c. c. of $N/100$-sodium thiosulphate required for 25 c. c. of the reaction mixture. As the concentrations of the reactants are equal, the velocity constant, k, has been calculated from the bimolecular formula,

$$k = 1/t \cdot \frac{x}{a(a-x)}$$

The results obtained are given in the following tables. Every experiment was repeated three or four times and the values of x given in the tables are the mean of three or four readings.

TABLES I.

Solvent—water.

t	...	4	24	44	64	84	104	114
x	...	0·64	3·61	6·19	8·41	10·35	12·10	13·65
$k \times 10^4$	...	64	64	64	63	62	62	62
							Mean	63

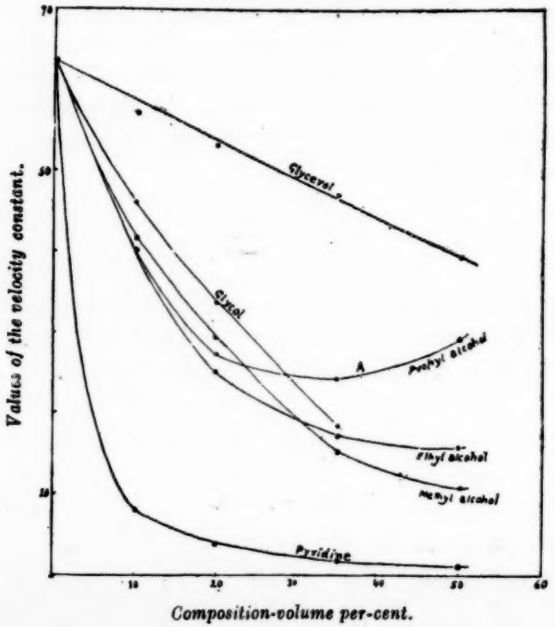
TABLE II.

Mean values of $k \times 10^6$

Organic solvents.	0%	10%	20%	35%	50%
Methyl alcohol ...	63·0	41·0	29·0	15·0	10·4
Ethyl alcohol ...	,,	40·0	25·0	17·0	15·5
Propyl alcohol ...	,,	40·0	27·0	24·0	29·0
Glycol ...	,,	45·7	33·3	18·1	—
Glycerol ...	,,	57 0	53·0	47·0	39·0
Pyridine ...	,,	7·6	3·7	1·6	1·0

The velocity constants have been plotted against the composition of the mixed solvents and the curves obtained are shown in Fig. 1. The percentage of the organic solvents higher than 50 could not be used due to the considerable decrease in the solubility of potassium persulphate in such mixtures.

Velocity constant—composition curves.
(Potassium persulphate-iodide)



(FIG. 1)

It will be seen from Table II that the addition of the organic solvents to water, retards the reaction between persulphate and the iodide ions in water; the retardation is greater with greater percentage of the organic solvents in the mixture. But propyl alcohol behaves slightly in a different manner. The velocity constant decreases with the increase in the propyl alcohol content of the mixture up to a certain concentration only ; higher concentrations than this increase the velocity constants (*cf.* a minimum point in the curve A Fig. 1).

The velocity constant—composition curves in mixtures containing methyl, ethyl and propyl alcohols, cut each other below 35 per cent. content of the alcohols but in mixtures containing more than 35 per cent. of these substances, the retarding influence decreases in the following order:—

$$CH_3OH > C_2H_5OH > C_3H_7OH$$

Increase of the hydroxyl groups in the molecule of the organic solvents also decreases the retarding effect.

Organic solvent.	Number of (OH) groups.	Percentage of the organic solvents.			
		10	20	35	50
Methyl alcohol ...	1	41·0	29·0	15·0	10·4
Glycol ...	2	45·7	33·3	18·1	—
Glycerol ...	3	57·0	53·0	47·0	39·0

Potassium persulphate is fairly soluble in water but insoluble in alcohols. But the decrease in the velocity constant is not in any way due to the decrease in the solubility of potassium persulphate by the addition of the organic solvents as in all the experiments the amount of potassium persulphate used was much smaller than that required for the saturated solution of potassium persulphate in water at 25°. Also in no experiment any precipitation of the solutes was observed. There is also no decrease in the concentration of potassium persulphate due to the oxidation of the organic solvents by the persulphate. For in some experiments potassium persulphate was kept in contact with the alcohols for two hours before adding to the potassium iodide solution and the mean velocity constant obtained in such an experiment was the same as obtained by mixing the two solutions immediately.

Buchbock (*Z. physikal. Chem.*, 1897, **23**, 123) has suggested that an increase in the viscosity of the solvent decreases the rate of reaction. But it will be seen from Table II that the velocity constants in glycerine-water and glycol-water mixtures are greater than alcohol-water and pyridine-water mixtures contrary to the above suggestion. Also the viscosities of the alcohol-water mixtures are maximum at certain compositions and therefore the velocity constants should be minimum at those concentrations. No minimum point has been observed in the present investigation in mixtures of methyl and ethyl alcohols ; a minimum point has only been observed in the case of propyl alcohol but not at the composition of the maximum viscosity. It appears probable that the viscosity of the medium does not exercise any appreciable influence on the rate of reaction. Bhonson (*loc. cit.*) has also come to similar conclusions.

The dielectric constants of organic solvents and of their mixtures with water are lower than that of water. Salzar (*Anal. Fis. Quim.*, 1924, **22**, 275) has found that the dielectric constant composition curves of the mixtures are straight lines and show discontinuities at compositions of certain hydrates of alcohols. The velocity constants of a reaction in pure organic solvents and in their mixtures with water will, according to Nernst-Thomson rule, be lower than in pure water. Although this has been found to be the case, yet the velocity constant—composition curves are not straight lines showing that there exists no direct proportionality between the velocity constants and the dielectric constants and that the dielectric constant is not the only factor influencing the rates of reaction.

Another important factor which exercises an influence on the velocity of the reaction is the molecular association of the solvents (*cf.* Cashmore, etc., *loc. cit.*). The minimum point observed in the case of propyl alcohol corresponds to the hydrate $C_3H_7OH \cdot 8H_2O$, the existence of which has already been shown by Christainsen (*Z. physikal. Chem.*, 1917, **92**, 257). It is possible therefore that alcohols producing the alcohol hydrates in the mobile state bring about a change in the regular behaviour of the mixtures at the particular composition.

It cannot therefore be said at present as to which is the deciding factor in controlling the velocity of a reaction in mixtures of organic solvents with water. Recently this reaction has been studied by Kiss and Hatz (*Rec. trav. chim.*, 1929, **48**, 7), in mixtures of methyl and ethyl alcohols and glycerol with water and they have also found

that the addition of these substances lowers the speed of the reaction and that no simple relation exists between the velocity constants and the concentration of the non-electrolytes. Also these workers could not find any relationship between the dielectric constants of the mixtures and the velocity constant of the reaction.

Summary.

1. The reaction between potassium persulphate and potassium iodide has been studied in water and in mixtures of water with methyl, ethyl, and propyl alcohols, glycol, glycerol and pyridine.

2. All the organic solvents retard the reaction: the retardation is greater as the concentration of these solvents in the mixture is increased.

3. A minimum point in the velocity constant—composition curve occurs in the case of propyl alcohol.

4. Increase of OH-groups decreases the retarding effect.

5. There is no relation between the velocity constant and the dielectric constants or the viscosities of the mixtures.

The authors wish to convey their thanks to Mr. S. M. Mehta, M.Sc., for his help during the progress of this work.

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Studies on the Complexes of the Chlorides of Gold with Organic Sulphides.

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Philips (*J. Amer. Chem. Soc.*, 1901, **23**, 257) studied the action of methyl sulphide on the chlorides of palladium, copper and gold and found that cupric chloride and auric chloride break down into the lower valency products, yielding $AuCl(CH_3)_2S$ and $[CuCl\cdot(CH_3)_2S]_2$ respectively. In the case of palladium, the author used palladious chloride and there was no further reduction. Herrmann (*Ber.*, 1905, **38**, 2813) studied the action of dibenzylsulphide on gold chloride and obtained two compounds, $AuCl\cdot(C_7H_7)_2S$ and $AuCl_2\cdot(C_7H_7)_2S$, named as aurodibenzyl-sulphinchloride and auric-dibenzylsulphide-dichloride respectively. The study of the above compounds shows that the organic sulphides have got a reducing action on gold chloride which latter combines with these sulphides only in the aurous state. It occurred to us whether this reduction could anyhow be prevented and whether it was possible to make gold chloride combine directly with the sulphides giving rise to the formation of compounds of the type $AuCl_3\cdot R_2S$ (R=an alkyl group).

According to the law of mass action, in the system,

$$AuCl_3 \rightleftharpoons AuCl + Cl_2$$

the active mass of chlorine should be increased in order to minimise the decomposition of auric chloride. This was attained by the use of a mixture of nitric acid (*d* 1·4, 1 vol.) and hydrochloric acid *d* 1·2, 1 vol.). The reactions were all exothermic, hence they took place better when the reaction vessels were cooled in ice.

The following compounds have been prepared as a result of these reactions:

1. (*a*) $AuCl_3\cdot(CH_3)_2S$ (*b*) $AuCl\cdot(CH_3)_2S$ (*loc. cit.*)
2. $AuCl_3\cdot(C_2H_5)_2S$

3. $AuCl_3 \cdot (C_3H_7)_2S$
4. $AuCl_3 \cdot \{(CH_3)_2 \cdot CH \cdot CH_2\}_2S$
5. (*a*) $AuCl_3 \cdot CH_3 \cdot S \cdot C_3H_7$ (*b*) $AuCl \cdot CH_2 \cdot S \cdot C_3H_7$
6. (*a*) $AuCl_3 \cdot (C_7H_7)_2S$
   (*b*) $Au_2Cl_4 \cdot 2(C_7H_7)_2S$ (*loc. cit.*)
   (*c*) $AuCl \cdot (C_7H_7)_2S$ (*loc. cit.*)

The preparation of compounds of the type $AuCl_3 \cdot R_2S$ in the pure state was very difficult in the case of sulphides containing a methyl or substituted methyl group, *e.g.*, Me_2S, $Me \cdot S \cdot Pr$, $(Ph \cdot CH_2)_2S$; for these have got a great tendency to form aurous compounds very readily, so that they are generated simultaneously during the preparation of the former; compounds of both types having very nearly similar solubility could not be separated from one another by fractional crystallisation. If in these cases the product be kept in contact with dilute aqua regia for several minutes, the mixture is converted into $AuCl_3 \cdot R_2S$. In the case of higher sulphides, *e.g.*, diethyl, dipropyl, *iso*butyl sulphides etc., compounds of the type $AuCl_3 \cdot R_2S$ were readily obtained while the preparation of the lower-valency products presented much difficulty.

Constitutional Formulæ.

Philips (*loc. cit.*) represented his compound, $AuCl \cdot (Me)_2S$ by the structural formula $Cl \cdot Au : S : Me_2$ while Herrmann suggested the formulæ $AuCl \cdot (C_7H_7)_2S$ or $Au \cdot S(C_7H_7)_2Cl$ for the compound aurodibenzylsulphinechloride as named by him. Of these two formulæ, the first is more reasonable. The chemical reactions of compounds of this type show that the chlorine atom always remains attached to gold. They react with ammonia and pyridine, forming $AuCl \cdot NH_3$ and $AuCl \cdot Py$. As the chlorine atom in these compounds is non-ionisable and the co-ordination number of gold in auro-compounds is 2, they can be conveniently represented by the general formula $\left[Au\begin{matrix} Cl \\ SR_2 \end{matrix} \right]$.

Compounds of the type $AuCl_3 \cdot R_2S$ are monomolecular, and nonconducting in freshly prepared acetone solution. Hence they can be represented as $\left[\begin{matrix} Cl \\ Cl \end{matrix} Au\begin{matrix} Cl \\ SR_2 \end{matrix} \right]$, the co-ordination number being four.

The constitution of the compound $Au_2Cl_4 \cdot 2(C_7H_7)_2S$ is somewhat interesting. This was isolated by Herrmann (*loc. cit.*) who determined its molecular weight in chloroform solution by the ebullioscopic method and found it lying between 607 and 608, instead of 482 (if the compound be monomolecular) and 964 (if the compound be dimolecular). He could not account for this anomalous result. Probably he could not prepare the compound in the pure state for its melting point is reported as 127° whereas we found it to be 133°. Determination of the molecular weight of the compound in benzene solution by the cryoscopic method gave the value at 944 corresponding to the dimolecular formula. This observation suggests two alternative formulæ, namely,

$[Au \cdot 2(Ph \cdot CH_2)_2S].[AuCl_4]$ and

(I)

$[AuCl_3''(Ph \cdot CH_2)_2S \cdot AuCl(Ph \cdot CH_2)_2S]$

(II)

The first required the compound to be conductive and the second, to be non-conductive, and actually it was non-conductive in freshly prepared acetone solution, though the conductivity changes gradually with time due to the decomposition of the compound and other disturbing factors, thus supporting the second formula.

Potassium thiocyanate reacts in the cold with $AuCl_3 \cdot R_2S$, liberating the alkyl sulphide group with the formation of potassium-aurithiocyanate, but this reagent has no appreciable action on $AuCl \cdot R_2S$ in the cold. $Au_2Cl_4 \cdot 2(C_7H_7)_2S$ was resolved by taking advantage of this reaction, keeping it in aqueous suspension and treating with potassium thiocyanate solution. The reaction took place as follows:

$$[AuCl(C_7H_7)_2S \cdot AuCl_3(C_7H_7)_2S] + 4KSCN$$
$$= AuCl(C_7H_7)_2S + 3KCl + KAu(SCN)_4 + (C_7H_7)_2S.$$

The products of the reaction, potassium aurithiocyanate, $AuCl \cdot (C_7H_7)_2S$ and benzylsulphide were separated from one another and obtained in the pure state (*vide* Experimental). The synthesis of the compound from $AuCl \cdot (C_7H_7)_2S$ and $AuCl_3 \cdot (C_7H_7)_2S$, as well as its resolution into these two products confirm, without doubt, the second formula suggested above.

The solution of the compound in acetone or chloroform liberates iodine from potassium iodide turning iodized starch-paper blue. This reaction indicates the presence of $AuCl_3 \cdot (C_7H_7)_2S$ as a component part of the compound for this latter only gives the same reaction, while $AuCl \cdot (C_7H_7)_2S$ has got no action on iodized starch-paper.

Lastly, the constitution may be supported from another point of view. The compound Au_2Cl_4—auroauric chloride (J. Thomson, *J. pr. Chem.*, **37**, 105)—is known and its constitution definitely established as $AuCl \cdot AuCl_3$. Now, since $(C_7H_7)_2S$ forms both $AuCl \cdot (C_7H_7)_2S$ and $AuCl_3(C_7H_7)_2S$ with $HAuCl_4$, it is expected that it will form $AuCl(C_7H_7)_2S \cdot AuCl_3(C_7H_7)_2S$—the dibenzyl sulphide compound of auroauric chloride.*

Properties.

Aurichloride dialkyl sulphides form yellow, prismatic crystals, aurochloride dialkyl sulphides are white, needle-shaped crystals, and auroaurichloride dibenzylsulphide is fine orange, silky, glistening crystals. The compounds have sharp melting points. They are soluble in most common organic solvents and are crystallisable from suitable media. They are non-conducting and monomolecular. The compounds of the type $AuCl \cdot R_2S$ react with bases like pyridine and ammonia, giving rise to the products $AuCl \cdot NH_3$ (Herrmann, *Ber.*, 1905, **38**, 2813) and $AuCl \cdot Py$, *i.e.*, the bases replace the sulphide molecules. The reactions are similar to the replacement of water molecule in salt-hydrates by ammonia and amines to form co-ordination compounds.

The compounds of the type $AuCl_3 \cdot R_2S$ react with potassium thiocyanate and potassium thiocarbamide to form potassium auricthiocyanate and chloroaurothiocarbamide (Moir, *J. Chem. Soc.*,

*We suggest the following *nomenclature* for the complex gold compounds :—

$AuCl \cdot R_2S$—aurochloride dialkyl sulphide (*cf.* $PtCl_4 \cdot 2(C_2H_5)_2S$—platochloride diethyl sulphide, Klason, *Ber.*, 1895, **28**, 1499; *J. pr. Chem.*, **1903**, *ii*, **67**, 19; $PtCl_2 \cdot 2(CH_3)_2S$—platochloride dimethyl sulphide, *J. pr. Chem.*, 1888, *ii*, **38**, 359; Klason, *ibid*, 1903, **67**, 24); $AuCl_3 \cdot R_2S$—aurichloride dialkyl sulphide (*cf.* $PtCl_4 \cdot 2(C_2H_5)_2S$—platichloride diethylsulphide and $PtCl_4 \cdot 2(C_3H_7)_2S$—platichloride dipropyl sulphide, Weibuk, *Z. Kryst.*, 1888, **11**, 142).

$Au_2Cl_4 \cdot 2(C_7H_7)S$—auroaurichloride dibenzyl sulphide (The name auridibenzylsulphide dichloride, as suggested by Herrmann, should therefore be rejected considering the arguments on which the constitution of the compound is based.)

1906, **105**, 164), according to the following reactions.

$$AuCl_3 \cdot R_2S + 4KSCN = KAu(SCN)_4 + 3KCl + R_2S$$

$$AuCl_3 \cdot R_2S + 2CS(NH_2)_2 = \begin{matrix} NH_2 \\ NH \end{matrix} \!\!> C \cdot S \cdot AuCl \cdot S \cdot C <\!\! \begin{matrix} NH_2 \\ NH \end{matrix} + 2HCl.$$

The liberation of hydrogen chloride was detected by the action of the solution on litmus paper and also by the formation of dense white fumes of ammonium chloride with ammonia. The liberation of alkyl sulphides was detected by the characteristic odour of the respective sulphides. In the case of $AuCl_3 \cdot (Ph \cdot CH_2)_2S$, the liberated dibenzylsulphide was actually isolated.

The compounds $AuCl_3 \cdot R_2S$ and $AuCl \cdot R_2S$ are interconvertible. The former is transformed into the latter by warming with alcohol and conversely the latter is converted into the former by treatment with dilute aqua regia or chlorine water. In the case of the complexes with benzylsulphide, the transformation takes place with formation of the intermediate product auroaurichloride dibenzyl sulphide. When the white aurochloride dibenzyl sulphide is treated with dilute aqua regia, it first changes to orange and finally to yellow; again the yellow aurichloride dibenzyl sulphide, on warming with alcohol for sometime on the water-bath, first passes through the orange state, ultimately becoming perfectly white, the crystals of $AuCl \cdot (C_7H_7)_2S$ separating. The compound, $Au_2Cl_4 \cdot 2(C_7H_7)_2S$ has actually been synthesized from $AuCl \cdot (C_7H_7)_2S$ and $AuCl_3 \cdot (C_7H_7)_2S$ by dissolving them in chloroform and crystallising from the same medium.

It may be asked whether $Au_2Cl_4 \cdot 2(C_7H_7)_2S$ is actually a compound or a mixture of $AuCl \cdot (C_7H_7)_2S$ and $AuCl_3 \cdot (C_7H_7)_2S$ in equimolecular proportions. A good amount of evidences can be put forward to prove the validity of its being a compound. When $AuCl \cdot (C_7H_7)_2S$ and $AuCl_3 \cdot (C_7H_7)_2S$ are intimately mixed up, the mixture is not orange; only the yellow colour of the auric complex become lighter due to the presence of the white auro-compound the melting point of the mixture is tardy (between 115° and 120°), lower than that of either of the constituents (m.p. of $AuCl(C_7H_7)_2S = 125°$, m.p. of $AuCl_3(C_7H_7)_2S = 118°$). But when the mixture is treated with chloroform or benzene, it immediately turns orange and gradually goes into solution. When this orange compound was crystallised from chloroform, it melted sharply at 133°, $Au_2Cl_4 \cdot 2(C_7H_7)_2S$,

obtained directly from gold chloride and benzyl sulphide also having the same melting point. The identity of the two compounds prepared by two entirely different methods leave no reason of doubt as to the validity of its being a compound. The double molecular weight of the compound also furnishes further evidence in its support.

Experimental.

Formation of Aurichloride dimethyl sulphide, $AuCl_3(CH_3)_2S$.

Chloroauric acid (10 g.) was dissolved in 5 c.c. of water and 1 c.c. of the acid mixture (nitric acid, *d* 1·4, 1 vol. + hydrochloric acid, *d* 1·2, 1 vol.) was added to this solution. The solution was cooled in an ice-bath and after 10 minutes methyl sulphide (0·5 g.) dissolved in 5 c.c. of acetone was added to the solution gradually (1 c.c. at a time, at intervals of 3—5 minutes). Each time as soon as the methyl sulphide was added, there was an evolution of heat and a heavy orange liquid separated which immediately changed to an orange-yellow precipitate. Some amount of white aurochloride dimethyl sulphide appeared simultaneously. On allowing the product to remain in contact with a further quantity of the acid mixture the formation of $AuCl_3 \cdot (CH_3)_2S$ became complete.

The mixture was filtered after half an hour and washed with an acid mixture consisting of *N*/10-HCl and *N*/10-HNO_3 (1 : 1) and then with water and finally with alcohol. It was next dried in air and crystallised from chloroform-ether mixture from which it separated as yellow prismatic crystals, m.p. 160°. The compound was soluble in chloroform, ether, acetone, warm benzene, etc., (Found: Au, 54·11; Cl, 29·09; S, 8·28. $AuCl_3(CH_3)_2S$ requires Au, 53·9; Cl, 29·13; S, 8·75 per cent.).

Formation of Aurochloride dimethyl sulphide, $AuCl(CH_3)_2S$.

This compound was prepared by Philip's method directly from gold chloride as well as by the reduction of aurichloride methyl sulphide by warming with alcohol on the water-bath. Instead of using alcoholic or ethereal solution of aurichloride as recommended by Philip, the aqueous solution was found to give greater yield. The proportions of gold chloride and methyl sulphide used were 1 : 3. The substance melted at 120°. (Found: Au, 27·13; Cl, 12·08;

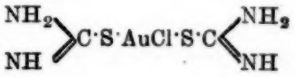
C, 8·12; H, 2·2. $AuCl(CH_3)_2S$ requires Au, 66·9; Cl, 12·06; C, 8·59; H, 2·1 per cent.)

Formation of the Compound, $AuCl{\cdot}C_5H_5N$.

One gm. of $AuCl{\cdot}Me_2S$ was warmed with 6 c.c. of pyridine on the water-bath for 15 minutes. The compound went into solution with slight decomposition, metallic gold separating out. It was next filtered, the reduced gold being removed thereby. The solution was next treated with ether when $AuCl{\cdot}C_5H_5N$ was precipitated as a white crystalline precipitate. The compound was very slightly soluble in alcohol and insoluble in other common organic solvents. It melted at 250-252° with slight decomposition. (Found: Au, 63·85; Cl, 11·39; N, 4·43. $AuCl{\cdot}C_5H_5N$ requires Au, 63·24; Cl, 11·36; N, 4·49 per cent.)

Formation of Aurichloride diethyl sulphide, $AuCl_3(C_2H_5)_2S$.

Gold chloride (8 g.) was dissolved in 2 c.c. of water, and 1 c.c. of nitric acid (*d* 1·4) was added to it. Ethyl sulphide (1·2 g.) dissolved in acetone (5 c.c.) was added to this solution. The mixture was thoroughly shaken and cooled in ice. Beautiful yellow prismatic crystals separated out of the orange heavy liquid which first separated after the addition of ethyl sulphide. These were filtered and washed with alcohol and ether and were recrystallised from dilute acetone, m.p. 95°. The properties were similar to those of the other compounds of this type. This was however found to be the most unstable compound of the series $AuCl_3{\cdot}R_2S$. It could be kept only two or three days after its preparation. (Found: Au, 49·78; Cl, 26·74 per cent. M. W. in benzene, 382. $AuCl_3(C_2H_5)_2S$ requires Au, 50·06; Cl, 27·06 per cent. M.W., 393·5).

Formation of Chloroaurothiocarbamide, 

The substance (4·35 g.) was held in suspension in alcohol, in which the compound was slightly soluble and an alcoholic solution of thiocarbamide (1 g.) was added to it gradually. The yellow substance immediately turned orange, and gradually went into solution which was colourless. It was next allowed to evaporate in air.

Crystals of chloroaurothiocarbamide gradually separated from the solution: this was followed by the separation of unchanged thiocarbamide. The first crop was purified by recrystallisation from alcohol. This compound was also obtained from other aurichloride dialkyl sulphides. (Found: Au, 51·6; Cl, 9·2. $AuClC_2H_6N_4S_2$ requires Au, 51·5; Cl, 9·28 per cent.)

Formation of Aurichloride dipropyl sulphide, $AuCl_3(C_3H_7)_2S$.

Gold chloride (5 g.) dissolved in water (5 c.c.) was treated with two drops of nitric acid (*d* 1·4) and two drops of hydrochloric acid (*d* 1·2). Propyl sulphide (0·5 g.) was added to this solution at 0°, the mixture being continually teased with a glass rod. The heavy oily liquid that separated became sticky gradually, giving a granular precipitate at last. The precipitate was collected and washed with alcohol, water, and again with alcohol and ether (yield, 3 gm.).

This compound, unlike the other compounds of the series, was more soluble in ether and crystallised from the same medium. It was more stable than the ethyl sulphide compound and less sensitive to light; m.p. 80°. (Found: Au, 47·09; Cl, 25·12 per cent. M. W. in benzene, 419·1. $AuCl_3(C_3H_7)_2S$ requires Au, 46·7; Cl, 25·27; per cent. M. W., 421·5).

Formation of Potassium aurithiocyanate from $AuCl_3(C_3H_7)_2S$.

Aurichloride dipropyl sulphide (4 g.) was held in suspension in 3-5 c.c. of water and potassium thiocyanate (1 g.) dissolved in 5 c.c. of water was added to it. It was next teased with a glass rod against the side of the reaction tube. The yellow salt at once turned red. The reaction was complete within 5-10 minutes. The strong smell of propyl sulphide was noticed during the reaction. It was next filtered and the precipitate dried by pressing it between the folds of a filter paper. It was next dried in air and treated with chloroform and ether to remove any unchanged aurichloride dipropyl sulphide. This compound was soluble in most common organic solvents. It decomposed at once in presence of acetone, in which it was extremely soluble. The very same compound was prepared similarly from other compounds of this series. (Found: Au, 43·2; S, 26·87; K, 8·18. $KAu(SCN)_4$ requires Au, 43·1; S, 27·35; K, 8·31 per cent.)

Formation of Aurichloride isobutyl sulphide.

Gold chloride (4 g.) was dissolved in water (5 c.c.) and the solution acidified with 2 drops of nitric acid (*d* 1·4) and 2 drops of hydrochloric acid (*d* 1·2). It was next cooled and treated with *iso*butyl sulphide (1 c.c.). The mixture was thoroughly shaken, again cooled, and allowed to settle for fifteen minutes. The precipitate was collected and washed with alcohol (yield, about 3 g.). The compound was dried and crystallised from ether; m.p. 83°. (Found: Au, 43·86; Cl, 23·58 per cent. M. W. in benzene, 469·8. $AuCl_2(C_4H_9)_2S$ requires Au, 43·82; Cl, 23·7 per cent. M. W., 449·5).

Formation of Aurichloride methyl-n-propyl sulphide, $AuCl_3 \cdot S\begin{matrix}CH_3\\C_3H_7\end{matrix}$

Gold chloride (4·4 g.), dissolved in water (5 c.c.) and 1 c.c. of the acid mixture, was treated with methyl-*n*-propyl sulphide (1 c.c.). The resulting yellow precipitate was separated from the mother-liquor and washed as usual (yield, about 4 g.). The substance was crystallised from chloroform-ether ; m.p. 85°. (Found: Au, 50·39 ; Cl, 26·66. $AuCl_3 \cdot (CH_3)C_3H_7S$ requires Au, 50·06; Cl, 27·06 per cent.).

Formation of Aurochloride methyl-n-propyl sulphide, $AuCl \cdot S\begin{matrix}CH_3\\C_3H_7\end{matrix}$

Methyl-*n*-propyl sulphide (4 g.) was treated with a solution of gold chloride (4 g.), free from nitric acid, in 5 c.c. of water. A perfectly white precipitate was formed. The mixture was then cooled, filtered and washed with alcohol and ether. The substance was crystallised from alcohol. The white glistening needle-shaped crystals melted at 100-101°. (Found: Au, 61·43; Cl, 10·97. $AuCl \cdot C_4H_{10}S$ requires Au, 61·1; Cl, 11·00 per cent.).

Formation of Aurichloride dibenzylsulphide, $AuCl_3(C_7H_7)_2S$.

Gold chloride (10 g.) dissolved in 5 c.c. of water was treated with 3 c.c. of the acid mixture. The solution was then cooled in an ice-bath and then treated with benzyl sulphide (1·5 g.) in alcoholic solution. The mixture was thoroughly shaken. Two substances, one

being yellow and the other orange, separated out. The mother-liquor was immediately decanted off and the pasty precipitate was at once treated with aqua regia (3-5 c.c.). When the whole mass became perfectly yellow, the mixture was diluted with a large excess of water, filtered and washed successively with the acid mixture, water, alcohol and ether and finally crystallised from benzene. Aurichloride dibenzyl sulphide is fairly soluble in acetone, chloroform and benzene and slightly soluble in alcohol, ether and other common organic solvents. It is very unstable in solutions, fairly stable only in the benzene medium; m.p. 118°. (Found: Au, 38·21; Cl, 31·97. $AuCl_3(C_7H_7)_2S$ requires Au, 38·07; Cl, 32·4 per cent.)

Formation of Auroaurichloride dibenzyl sulphide, $Au_2Cl_4.2(C_7H_7)_2S$.

This compound was prepared by the method recommended by Herrmann (*Ber.*, 1905, **38**, 2813) by treating an ethereal solution of gold chloride (2 mol.) with an ethereal solution of benzyl sulphide (1 mol.). The compound was purified by repeated crystallisation from chloroform. The above compound had been synthesized from aurochloride dibenzyl sulphide and aurichloride dibenzyl sulphide. When these two substances were mixed in equimolecular proportions in chloroform and crystallised from the same medium, beautiful, orange, silky, prismatic crystals separated out; m.p. 133°. (Found: Au, 40·7, 40·57; Cl, 14·67, 14·57 per cent. M.W. in benzene, 944. $Au_2Cl_4{\cdot}2(C_7H_7)_2S$ requires Au, 40·87; Cl, 14·73 per cent. M.W., 964).

Interaction of KSCN *and* $Au_2Cl_4{\cdot}2(C_7H_7)_2S$.

By this important reaction, aurcaurichloride dibenzyl sulphide was resolved into its components, which elucidated the doubtful constitution of the molecular compound.

About 4 gms. of the auroauric compound in aqueous suspension were treated with 1 gm. of potassium thiocyanate in 5 c.c. of water. The mixture was then teased with a glass rod against the sides of the reaction tube. The orange colour of the substance deepened into brick red. The product was then filtered and immediately washed several times with water in order to remove unchanged potassium thiocyanate and the potassium chloride formed during the reaction. The precipitate consisting of $KAu(SCN)_4$, $AuCl(C_7H_7)_2S$ and dibenzylsulphide was dried at the ordinary temperature and extracted

several times with ether to remove dibenzylsulphide and then with chloroform to remove $AuCl(C_7H_7)_2S$. On concentrating the ethereal and chloroform solutions, a residue was obtained which on fractional crystallisation from chloroform and ether gave substances which on analysis were found to be pure benzylsulphide (m.p. 50°) and pure $AuCl(C_7H_7)_2S$ (m.p. 125°). The substance left after the above treatment was pure potassium aurithiocyanate. (Found: Au, 42·42; K, 8·27. $KAu(SCN)_4$ requires Au, 42·1; K, 8·33 per cent.) (Found: Au, 43·95. $AuCl(C_7H_7)_2S$ requires Au, 44·12 per cent.)

Formation of Aurochloride dibenzylsulphide, $AuCl(C_7H_7)_2S$.

The compound was prepared by Herrmann (*loc. cit.*) by warming auroaurichloride dibenzylsulphide with ethyl alcohol on the water-bath. It was found possible to prepare this compound directly from benzylsulphide and gold chloride without passing through the intermediate compound $Au_2Cl_4 \cdot 2(C_7H_7)_2S$, if instead of adding benzyl sulphide to gold chloride, the aqueous solution of the latter be poured cautiously, into a large excess of benzylsulphide in alcohol. First, the mixture became yellowish, but in 15-20 minutes, it became perfectly white. It was then filtered and washed with alcohol and ether. Herrmann observed that the compound, he prepared, when exposed to air, became yellowish. This was probably due to the presence of traces of $Au_2Cl_4 \cdot 2(C_7H_7)_2S$ in the compound, as an impurity. For the pure compound that we obtained was very stable. It could be kept for months together without decomposition or any change of colour. The melting point given by Herrmann is 122°, whereas our compound melted at 125°. This also indicates the presence of impurities in his compound. (Found: Au, 44·11; Cl, 8·05. $AuCl \cdot (C_7H_7)_2S$ requires Au, 44·12; Cl, 7·95 per cent.).

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Stereochemistry of Some Alicyclic Ring-Systems. A Preliminary Note.

By Muahammad Qudrat-i-khuda.

The recent investigations of Hückel and his collaborators (*Annalen*, 1925, **441**, 1, and subsequent papers) on the strainless nature of the decahydronaphthalene ring raise the question whether simpler monocyclic ring-systems also possess a similar strainless configuration as suggested by Sachse (*Ber.*, 1890, **23**, 1363), and developed later on by Mohr ((*J. pr. Chem.*, 1918, **98**, 315; 1922, **103**, 316). According to them, one would expect that monosubstituted *cyclo*hexane derivatives should exist in two stereoisomeric forms, while disubstituted *cyclo*hexane compounds would be capable of existing in four isomeric modifications according as the *cyclo*hexane ring possessess the boat-(Fig. I) or the chair-(Fig. II) shaped configuration.

Fig. I.

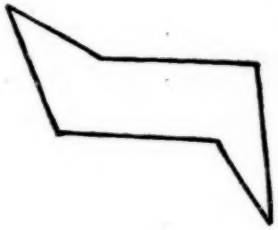
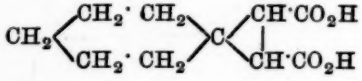


Fig. II.

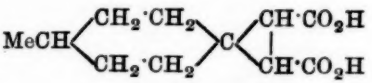
But up till now, no evidence of such compounds appears to have been recorded in the literature. On the other hand, the experimental observations, on purely chemical ground, suggest that *cyclo*hexane is a monoplanar ring; in fact the unusual stability of *cyclo*hexane-*spirocyclo*propane-2:3-dicarboxylic acid (I) led Beesely, Ingold and Thrope (*J. Chem. Soc.*, 1915, **107**, 1080) to discard the hypothesis of the strainless *i.e.* the multiplanar configuration

of the *cyclo*hexane ring and to assume that it has a uniplanar arrangement. Later on Baker and Ingold (*J. Chem. Soc.*, 1923, **123**, 122) observed that *cyclo*heptane ring exerts an influence which cannot be explained on the assumption of the monoplanar configuration for it. And this led them to reconsider the matter and finally to accept the views of Sachse and Mohr on the subject, with this modification that while *cyclo*heptane and higher-membered rings behave like true strainless system, the *cyclo*hexane molecule is a vibrating framework of the two strainless forms (Figs. I and II) and the resultant effect exerted by it is similar to that of a uniplanar ring. If this were the case, one would expect that by introducing substituents at any two carbon atoms of the *cyclo*hexane ring, the free vibration of the molecule would be prevented to some extent and it may then be possible to obtain evidence in support of the multiplanar configuration of the ring; and in this connection it is proposed to undertake the elucidation of the following points, namely:

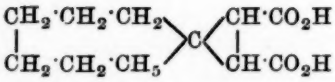
(*i*) An examination of the stability of the *cyclo*propane ring in *p*-methyl*cyclo*hexane-*spirocyclo*propane-2:3-dicarboxilic acid (II) will be made in order to see, if the stability is of the same order as that of *cyclo*hexane-*spirocyclo*propane-2:3-dicarboxylic acid (I) or similar to those of its *cyclo*heptane and *cyclo*pentane analogues (III) and (IV) respectively.



(I)



(II)



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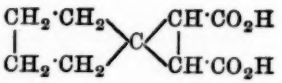
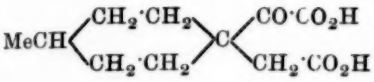


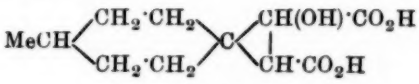
(IV)

(*ii*) To synthesise the ketoglutaric acids similar to *p*-methyl-*cyclo*hexane-1-oxalyl-1-acetic acid (V), and to study the action of concentrated caustic potash solution on it, to find out whether like

its *cyclo*hexane analogue, it passes into the *cyclol*-derivative (VI) or is stable like the corresponding *cyclo*pentane compounds.



(V)



(VI)

(*iii*) To examine whether by increasing the number, as well as the molecular volume of the substituents, it is possible to isolate the number of stereoisomeric forms of the same compound, as necessitated on the assumption of the strainless configuration.

(*iv*) To examine whether a monocyclic ring-system is capable of of being interconvertible into a higher or a lower membered ring and if so with what ease and to what extent the interconversion can be effected (*cf.* Meerwein and Schafer, *J. pr. Chem.*, 1922, *ii*, **104**, 289).

In the case of *p*-methyl*cyclo*hexanone, some interesting results have already been obtained ; the work, however, is not yet complete. A detailed description of it will be published later on. In the mean time for various reasons, it seemed desirable to publish a preliminary note on the subject.

In this connection, I desire to express my indebtedness to Professor J. F. Thorpe, C.B.E., F.R.S., for allowing me to carry on this work, which is so much allied to his classical researches on the stability of *spiro*-compounds.

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Jute Seeds—*Corchorus Capsularis*. Part III. Their Chemical Composition.

By Nirmal Kumar Sen.

In a previous communication (*J. Indian Chem. Soc.*, 1928, **5**, 759) an account was given of the composition of jute seed oil. It appeared, however, of importance and interest to extend the investigation by examining also the other constituents of the seeds.

The first chemical investigation of the seeds of *Chorchorus capsularis* was by Tsuno (*Monatsh. pr. Tierheilkunde*, 1895, **6**, 455), who indicated the presence of a bitter principle under the name of *corchorin*. The corchorin of Tsuno was a brown amorphous powder and turned bluish-green with concentrated sulphuric acid. But the glucoside obtained from the seeds of the same plant by the present author seemed to be different from corchorin as it was a white crystalline substance and developed a red colouration with sulphuric acid.

From all the data that are available regarding Tsuno's corchorin it appears that after all it was a highly impure specimen, from which no attempt was made to prepare any substance in a pure and crystalline condition. If may be mentioned here incidentally that a substance answering all the descriptions of Tsuno's corchorin was first obtained during the preliminary process of isolation of the bitter principle from the seeds of *Corchorus capsularis*. But on investigation, this product was subsequently resolved into a number of components amongst which a crystalline glucoside having an intensely bitter taste was found to be the essential principle. Contrary to the assertion of the previous investigators, this substance was found to be free from nitrogen and so it could not be an alkaloid as they had supposed.

Another pharmacological investigation relating to *Corchorus capsularis* has furthermore been recorded by Kobert (*Ber. Natur. Ges. Rostock* ; *Arch. Freund Natur. Ges. Mecklenburg*, 1906, No. 5; vide *Chem. Zentr.*, 1907, **1**, 1273) who had received the impure product from the firm of Merck for his experiment on animals. In this connection he described certain chemical and physical properties

of the subtance. But none of the workers made any statement regarding the isolation and purification of the bitter principle and there was no mention of its melting point and composition.

A still later publication embraces a study of *Corchorus capsularis* by Annett (*Biochem. J.*, 1917, **11**, 192) in which he stated that the seeds contained raffinose to the extent of about 2·25 per cent. but he made no statement concerning the other constituents of the seeds.

From the brief review of the literature it will be observed that no complete chemical examination has hitherto been made of jute seeds and nothing is known about the composition of the bitter principle which was considered to be the probable source of the reputed physiological action of the seeds which are used to some extent medicinally in India.

The bitter principle of jute seeds isolated by the present author was found to be a colourless substance crystallising in stout rhombic prisms, m. p. 174-175°. It had a molecular formula of $C_{22}H_{36}O_8$ and possessed an intensely bitter taste. Its character as a glucoside was proved by the fact that on hydrolysis by mineral acids it lost a molecule of glucose and was converted into another substance of alcoholic character.

Saha and Chowdhury (*J. Chem. Soc.*, 1922, **121**, 1044) described a compound under the name of *capsularin* which they obtained from the leaves of the same plant having the same molecular formula and melting point as the corchorin isolated by the present author from the seeds of the same plant. But the most interesting thing about corchorin is that it is dextrorotatory $[\alpha]_D = +33{\cdot}4$, whereas capsularin is leavorotatory $[\alpha]_D = -23{\cdot}6$. The former is insoluble in dilute mineral acids and is resinified when heated with 2% sulphuric acid without being hydrolysed whereas the latter dissolves and is easily hydrolysed when heated with 2% sulphuric acid.

Though there appears to be little doubt that these compounds are closely related, the connection between them cannot be predicted with any reasonable certainty until sufficient data regarding their composition are forthcoming.

Experimental.

The material employed for this investigation was obtained through the kindness of Prof. J. C. Ghosh, D.Sc., who had specially procured a quantity of the seeds for the author from Mr. R. S. Fin-

low, Director of Agriculture, Bengal. The author had thus the assurance that the material was perfectly authentic.

Test for Alkaloid.—A portion of the crushed seeds (10 g.) when treated with Prollius fluid (*Arch. Pharm.*, 1882, **19**, 85) did not give any reaction for alkaloid.

Fermentation of the Seeds.—The seeds on soaking in water quickly began to ferment with evolution of gas. Preliminary examination showed that hydrogen and carbon dioxide were produced.

No fermentation of the seeds took place when they were treated with 2 per cent. copper sulphate solution and immersed in sterile water for a fortnight, nor when thymol was added to a mass of crushed seeds and water. The fermentation was therefore, due to bacteria.

Test for Enzyme.—A quantity (100 g.) of the ground seeds was macerated with distilled water at the ordinary temperature for three days with the addition of a little chloroform to prevent bacterial action. To the filtrate about three times its volume of 95 per cent. alcohol was added, when an abundant pale brown flocculent precipitate was produced. After standing for some time the precipitate was collected, washed successively with a little alcohol, ether and dried in *vacuo* over sulphuric acid. When dry it formed a brown mass which could be triturated to a grayish powder and amounted to 3·4 per cent. of the weight of the seeds employed.

The freshly prepared substance was at first capable of re-solution in water. Its aqueous solution was slightly trubid and did not give any colouration with ferric chloride but gave a flocculent white precipitate insoluble in acetic acid with lead acetate. It contained nitrogen and an acidified solution of the substance gave a white precipitate with potassium mercuric iodide. It did not hydrolyse amygdaline but when a little quantity of the substance was placed in a test tube and covered with a dilute solution of hydrogen peroxide a brisk evolution of oxygen took place thus indicating the presence of catalase.

Table I gives the proximate analysis of the seeds and Table II that of the ash.

TABLE I.

Moisture ...	7·1%	Crude fibre ...	20·76%
Ash	6·0%	Free invert sugar ...	3·079%
Protein (N. 6·25)	26·62%	Sugar by inversion ...	5·95%
	Starch trace.		

TABLE II.

Ash soluble in water	... 24·5%	P_2O_5	... 33·16%
Ash soluble in acid	... 74·2%	SiO_2 as sand	... 1·30%
Sand and silicate (by difference).	... 1·3%	Fe_2O_3	Traces, not estimated.
TOTAL	... 100·00	MgO	... 8·21%
Alkalinity of the ash (in terms of K_2CO_3).	... 9·25%	CaO	... 20·73%
		Al_2O_3	Not estimated.
		Na_2O	... 3·23%
		K_2O	... 25·45%
		SO_4	... 4·24%
		CO_2	Not estimated.
		Cl_2	Traces, not estimated.
		TOTAL	96·32%

Extraction with various solvents.—In order to ascertain the general character of the constituents, 50 gm. of the powdered seeds were extracted successively in a Soxhlet's apparatus with various solvents whereby the following amounts of extract, dried at 100° were obtained.

Petroleum ether (b. p. 40-60°) extracted				14·72%
Ether	...	...	,,	1·36%
Chloroform	...	...	,,	1·9%
Alcohol (95%)		...	,,	15·72%
Water	...	...	,,	7·1%
	Residue	...	...	56·00%
	Loss	...	..	3·2%
			TOTAL	100·00

Petroleum extract.—This extract contained a fatty oil—a detailed account of which had been given in Part II (*loc. cit.*).

Ether extract.—The extract, after the complete removal of the solvent, was a yellowish green viscous mass. It was re-dissolved in a large volume of cold ether whereby a small quantity of sparingly soluble substance was obtained.

The more readily soluble extract was a greenish viscous mass and was shaken up repeatedly first with an aqueous solution of sodium carbonate and then with dilute solution of caustic soda. The combined extracts were then extracted in acid solution with low boiling naphtha (30-50°). The small amount of nearly colourless fatty acid thus isolated was crystallised from alcohol and possessed the following constants : m. p. 30-32° ; neutralisation value 181·5; mean molecular weight 309·1 and iodine value 54·6 (Hubl's).

The ethereal solution, which had been extracted with aqueous sodium carbonate, was washed, dried and the solvent removed, when a small quantity of fatty oil was obtained, which would naturally be expected to be similar in composition to that obtained from the seeds by extracting with light petroleum ether. It was found to contain a very small quantity of sterols melting at 126·5-128°. The mixed fatty acids obtained on hydrolysis contained, like those obtained from the extracted oil, mixture of oleic, linoleic, palmitic, and stearic acids.

The sparingly soluble substance of the ether extract of the seeds was a crystalline brittle powder—the greater portion of it was found in the flask during the extraction of the seeds with ether. When purified from alcohol (animal charcoal) it was obtained as a white micro-crystalline powder, insoluble in water but soluble in warm 90 per cent. alcohol. It dissolved in concentrated sulphuric acid with a violet colour and its alcoholic solution gave a green colouration with ferric chloride and a white precipitate with alcoholic lead acetate solution. It was tasteless and did not contain nitrogen. On account of the very small amount of the material it could not be further investigated.

Chloroform extract.—This extract was a brown viscous mass from which no crystalline product could be isolated.

Alcoholic extract.—The residue from the chloroform extract of the seeds (a lot of 2·8 kilograms) was completely extracted with hot 95 per cent. alcohol in a Soxhlet's apparatus. The extract was concentrated under reduced pressure and allowed to stand. After a time lumps of crystalline mass (73 gm.) separated; these were collected, dissolved in warm water and filtered from oily and colouring matter. The filtrate was evaporated to a syrup under reduced pressure and the residue was dissolved in 90 per cent. boiling alcohol (animal charcoal), filtered and allowed to stand. On the following day glistening stout prismatic needles arranged in hemispherical masses

separated out which melted at 72-74°. It was very soluble in hot water and had a slightly sweet taste and did not reduce Fehling's solution. The substance, on hydrolysis with mineral acids readily reduced Fehling's solution. When heated in a dry test-tube it lost water of crystallisation and at 120° turned brownish yellow and its solution then reduced Fehling's solution. It gave Salivanoff's reaction and on boiling with concentrated hydrochloric acid gave a reddish-brown colouration.

The substance was dried in a desiccator over concentrated sulphuric acid at the ordinary temperature for 16 days during which about 14·22 per cent. of water was lost and the constant weight was obtained after 27 days when it lost 14·24 per cent. of water. The last trace of water of crystallisation was removed by drying it in *vacuo* in a toluene-bath in presence of phosphorus pentoxide and it showed to contain 14·94 per cent. water of crystallisation. It was dextrorotatory $[\alpha]_D = +109·3°$ and the molecular weight of the substance by the cryoscopic method was found to be 635.

Hydrolysis of the sugar.—5 Gm. of the substance were hydrolysed by heating with 3 per cent. sulphuric acid. It was then neutralised with barium carbonate and filtered. One half of the filtrate when heated with an alcoholic solution of *as*-methylphenylhydrazine yielded *d*-galctosemethylphenylhydrazone, m.p. 180°.

The other half of the hydrolysed product when slowly oxidised with nitric acid (sp. gr. 1·15) at 60° yielded mucic acid.

A portion of the neutral hydrolysed product gave a beautiful blue colouration with a saturated aqueous solution of ammonium molybdate in three minutes at 40°—thus indicating the presence of fructose in the hydrolysed product (Pinoff's test for fructose in presence of other sugars, *Chem. Ztg.*, 1914, **38**, 629).

It is evident from the above results that raffinose is present in the seeds of *Corchorus capsularis* and this observation is quite in accordance with that of Annett (*loc. cit.*) who obtained raffinose from jute seeds by precipitating it with ether from the alcoholic extract of the seeds.

On further standing, the alcoholic mother-liquor from which raffinose had been removed deposited a green mass. This was filtered and the residue was well washed with dilute alcohol. The slimy green residue was successively extracted with petroleum ether, ether and alcohol (90 per cent.). The alcoholic solution yielded a green soft waxy mass. It was crystallised from glacial acetic acid in

yellowish brown microscopic needles, m.p. 95-98° with decomposition. It was soluble in hot alcohol with a light green fluorescence, sparingly soluble in ether, insoluble in water, alkali and sodium bicarbonate solutions. It gave a beautiful violet colouration with ferric chloride and a white precipitate with lead acetate in alcoholic solution. It did not decolourise bromine. When heated on platinum foil it first melted and then burnt with a smoky flame without leaving any residue. It was tasteless and did not contain nitrogen. (Found: C, 68·83; H, 12·53. $C_{10}H_{22}O_2$ requires C, 68·96; H, 12·64 per cent.). There was not sufficient substance left to determine its molecular weight and further work is in progress.

Isolation of Corchorin.—The alcoholic filtrate after the removal of the solvent under reduced pressure yielded a thin dark brown viscous mass. This was mixed with water and subjected to distillation with steam until volatile matters ceased to pass over. A distillate was obtained which contained some white solid substance floating on the surface. The distillate was neutral to litmus and about two litres were collected. It was saturated with sodium chloride and extracted with ether, the ethereal solution being washed with water, dried with anhydrous sodium sulphate and the solvent removed. There was thus obtained a very small quantity (0·065 g.) of brownish semi-solid mass having a smoky odour. It did not give any colouration with ferric chloride. The amount was too small for further investigation.

After the removal of the volatile matter there remained in the distilling flask an aqueous liquid (A) and a small quantity of black resin (B).

As the greater portion of the resin (B) contained in the aqueous liquid was in too fine a state of division to admit of its separation by filtration, this was partially effected by decantation and it was subsequently well washed with water. The aqueous liquid which still possessed a milky appearance was treated with an excess of 10 per cent. solution of lead acetate, which produced a voluminous yellowish precipitate. This was collected on a filter, thoroughly washed with water, suspended in water and decomposed by hydrogen sulphide. On filtering the mixture a red liquid was obtained. The liquid was concentrated under reduced pressure and as it gave nothing crystalline on standing, was finally mixed with purified powdered pumice stone and successively extracted in a Soxhlet's appa-

ratus with ether, chloroform, ethyl acetate and alcohol. These solvents, however, did not effect the separation of any crystalline substance.

The filtrate from the lead acetate precipitate was treated with sulphuretted hydrogen for the removal of the excess of lead, filtered and the excess of sulphuretted hydrogen was removed in a current of carbon dioxide. The yellow sparkling filtrate was extremely bitter and contained a large amount of sugar since it readily reduced Fehling's solution and yielded an osazone, m.p. 202°.

The liquid, however, on standing deposited slowly a white sandy micro-crystalline powder having an extremely bitter taste. It was afterwards found that the filtrate on concentration and exposure to air for a few days yielded the same crystals. It was filtered, washed successively with water, absolute alcohol and ether and finally dried in *vacuo* over sulphuric acid. The yield was about 0·4 per cent. of the weight of the dry seeds.

After crystallisation from alcohol (animal charcoal) it was obtained in the form of colourless rhombic prisms, m.p. 174-175° and from dilute pyridine, after a week, in short prisms with rounded ends melting at the same temperature. It was sparingly soluble in water and chloroform, insoluble in ether but readily soluble in alcohol (95 per cent.). It dissolved in cold concentrated sulphuric acid with a red colour with green fluorescence and decolourised bromine in acetic acid solution in the cold. It was readily soluble in pyridine and acetic acid but insoluble in benzene. Its aqueous solution was neutral to litmus and was extremely bitter. The bitterness of the substance was so intense that it could be detected in 5 c.c. of water to which 0·1 c.c. of an one per cent. alcoholic solution of the substance had been added. A smaller quantity could not be detected by the bitter taste. The bitterness could be removed by shaking the aqueous solution several times with freshly ignited animal charcoal. By extracting the dried charcoal thus treated with hot absolute alcohol the bitter constituent could be recovered. It reduced ammoniacal silver nitrate in alcoholic solution but not Fehling's solution and turned potassium ferricyanide solution containing a little ferric chloride blue (Turnbull's blue). On warming with moderately strong mineral acids a light yellow solid separated out and the filtrate, after neutralisation reduced Fehling's solution on warming. The mixture after hydrolysis gave a fatty smell. The bitter could be salted out from a concentrated aqueous

solution by ammonium sulphate and was precipitated by tannic acid and basic lead acetate. By digesting the tannate of the glucoside with zinc oxide and extracting the mixture with alcohol, the bitter could be obtained in the alcoholic solution.

On heating the substance in an air oven for 24 hours at 110-112° it did not lose any weight thus indicating the absence of water of crystallisation in the substance. In a very finely divided condition it attacked the mucous membrane of the nose and produced violent sneezing. In alcoholic or aqueous solution it did not give any colouration with ferric chloride nor any precipitate with either copper acetate, lead acetate or silver nitrate. But when a little of the substance was dissolved in chloroform with acetic anhydride and a few drops of concentrated sulphuric acid subsequently added a blue colouration was produced which readily changed to green. It did not contain nitrogen. On heating on a platinum foil it first melted to a yellow liquid, charred and then completely burnt with a yellow and slightly sooty flame. It was dextrorotatory $[\alpha]_D = +33{\cdot}4$ in alcoholic solution. (Found: C, 61·6 ; 61·72 ; H,8·5, 8·6 per cent. M. W. cryoscopic in glacial acetic acid, 423, 427 and in phenol 435, 439. $C_{22}H_{36}O_8$ requires C, 61·68; H, 8·41 per cent. M. W. 428.)

The mother-liquor from which corchorin was separated was concentrated to a syrup. It gave no precipitate with potassium-mercuric iodide, iodine or phosphomolybdic acid thus showing the absence of any substance of alkaloidal nature.

With the object of ascertaining whether any definite hydrolytic product could be obtained from the substance, the syrup was heated for some time with moderately strong hydrochloric acid when a dark brown solid soon began to separate. After hydrolysis was complete the mixture was extracted with ether and the ethereal solution was first washed with aqueous sodium hydroxide to remove some colouring matter and subsequently with water, after which it was dried and the ether removed when a small quantity of a yellow solid remained. This was purified from alcohol when it melted at 114-115°. It was found to be the hydrolytic product of the glucoside corchorin and further work to elucidate its composition is in progress.

The syrup contained an abundance of sugar and in order to confirm the identity of the sugar a portion of the syrup was treated with ammoniacal lead acetate which gave a voluminous precipitate. On heating it assumed a salmon-pink colour. This was filtered,

washed with water, suspended in water and decomposed by sulphuretted hydrogen and filtered. The filtrate was carefully neutralised by sodium carbonate and clarified by animal charcoal. The filtrate readily reduced Fehling's solution and yielded *d*-phenylglucosazone, m. p. 203°, and this showed the presence of glucose in the seeds.

The Resin (B).

The black resinous material contained in the portion of the alcoholic extract, which had been separated from the aqueous liquid as above described was digested with alcohol, mixed with purified powdered pumice stone and the thoroughly dried mixture was extracted successively in a Soxhlet's apparatus with various solvents. Only chloroform and ethyl acetate extracts yielded crystalline substances.

Chloroform Extract of the Resin.—This extract was a dark brown solid, which was again dissolved in boiling chloroform and on slow evaporation of the solution a crystalline mass separated out which on further purification from alcohol yielded a colourless mass, m.p. 172-174° which was found to be identical with corchorin (*loc. cit.*).

Ethyl Acetate Extract of the Resin.—This extract was a deep brown solid, and on slow evaporation of the concentrated solution of the extract beautiful clusters of stout, rhombic, brown plates deposited. When powdered it was found to be brittle and white inside. When heated on the platinum foil it burnt with a sooty flame leaving no residue. It melted at 165-168° and was sparingly soluble in water and alcohol but readily soluble in nitrobenzene, methyl alcohol and pyridine. With concentrated sulphuric acid it gave a deep red colouration but no colouration with ferric chloride. Its aqueous solution was neutral to litmus and at first had an astringent taste but soon developed an after-bitter taste. As the substance obtained was very small it could not be analysed.

Effect of Corchorin on Red Blood Corpuscles.—The object of this experiment was to see whether the jute-seed bitter had any hemolytic action on red blood corpuscles. In the present experiment fresh and washed human corpuscles completely freed from serum by repeated centrifuging with normal saline was used. The red blood corpuscles were suspended in physiological saline. 2 C.c. of the suspended red blood corpuscles were taken in a test-tube and mixed

with a known amount of corchorin in a known volume of normal saline so that the combined volume was brought to a standard volume of 10 c.c. The contents of the two tubes were rapidly mixed three times and then allowed to rest first in a stand at the laboratory temperature and then in an incubator at 37°. For comparison a standard hemolysed tube prepared by adding a known amount of saponin in normal saline was used.

R.B.C.=2 c.c. Total volume=10 c.c.

Corchorin 0·1% in c.c.	0	0·5	1·0	2·0
Time.				
0	No effect.	No effect.	No effect.	No effect.
15 min.	,,	Slight ppt.	Slight ppt.	Slight ppt.
30 ,,	,,	,,	,,	,,
60 ,,	,,	,,	,,	,,
After 24 hours at 37°	Settles.	Completely settles.	Completely settles.	Completely settles.

The above result showed that corchorin was devoid of any hemolytic action on red blood corpuscles.

Bactericidal Action on B.Coli.—A fresh 24 hours culture of B. *coli* was kept suspended in a sterilised saturated solution of corchorin in normal saline. After 25 minutes, a drop of suspension was put in a fresh agar tube. After 24 hours *B.Coli* was seen to grow in the tube. This shows that the saturated solution of corchorin had no bactericidal effect on *B.Coli*.

The jute-seed oil and the bitter principle are now being submitted to further physiological tests.

Summary.

A more extensive investigation of the jute seeds has been undertaken. Preliminary examination shows that the seeds are rich in phosphates and potash. Water extracts 3·4 per cent. of a crude nitrogenous substance which has been found to contain the enzyme catalase.

The general character of the seeds has been determined by extracting the seeds with various solvents.

The petroleum extract which amounted to 14·72% of the whole contain a fatty oil, a detailed account of which has been given in Part II.

The ether extract amounted to 1·36% of the whole and consists of some fatty matter probably lecithin and a colourless micro-crystalline mass possessing phenolic properties.

The chloroform extract amounted to 1·9% and consists of brown resin from which nothing definite has been isolated.

The alcoholic extract which amounted to 15·72% is the more important product obtained from jute seeds and special consideration has therefore been given to the character of the product in the present investigation.

Raffinose has been obtained from this extract to the extent of about 3 per cent. thus confirming the observation of Annett.

Corchorin, ($C_{22}H_{36}O_8$) the active principle of the seeds has been isolated in a very pure form. It is a glucoside having an extremely bitter taste " ten times more bitter than quinine sulphate". It forms glistening rhombic prisms melting at 174-175° and has saponin-like properties but unlike saponin it has no hemolytic action on red blood corpuscles. It is dextrorotatory and the combustion and molecular weight determination indicate a cyclic alcohol. Further physical and chemical properties are being studied with a view to determine its constitution.

The alcoholic extract also yields two other products, one crystalline and another amorphous which have not yet been characterised.

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The Principles Underlying Aromatic Side-chain Reactivity from the Standpoint of the Electronic Theory of Valency.

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1. *Historical*: *Principles of Correlation and Inversion.*

Recent work on the effect of nuclear substituents on reactions in the side-chains of benzene derivatives has led to generalisations which pave the way to a theory of aromatic side-chain reactivity closely linked with the modern theory of nuclear aromatic substitution.

Some time ago Olivier demonstrated the existence of a relation between nuclear and side-chain reactivity, for the example of the latter represented by the acid hydrolysis of benzene chlorides (*Rec. trav. chim.*, 1922, **41**, 301, 646 ; 1923, **42**, 516, 775): the velocities of hydrolysis for three isomers of the form $R{\cdot}C_6H_4{\cdot}CH_2Cl$ were found to be in the order *o*, *p*$>$*m* or *m*$>$*o*, *p*, according as R belonged to the *op*- or *m*-orienting series ; and, moreover, the facilitating or retarding action of different groups R exhibited a close parallelism to their influence on reactivity in ordinary nuclear substitution. Similar relationships have since been established for several other side-chain transformations, including the condensations of benzyl chlorides with benzene in the presence of aluminium chloride, the saponification of benzoic esters, the addition of hydrogen sulphide to benzonitriles, and bromination in a methyl side-chain (Olivier and Berger, *ibid.*, 1926, **45**, 710 ; 1927, **46**, 605 ; Kindler, *Annalen*, 1926, **450**, 1 ; Ingold and Rothstein, *J. Chem. Soc.*, 1928, 1217).

It is known, however, that there is another group of side-chain reactions for which the above relations become to a large extent inverted. Lapworth, Shoesmith and others have found (*J. Chem.*

Soc., 1922, 1391 ; 1924, 1312, 2278 ; 1926, 214) that the two groups of nuclear substituents for which the ease of acid hydrolysis of isomeric benzyl halides are respectively in the order *o*, *p*>*m* and *m*>*o*, *p*, become interchanged (with the exception of chlorine and bromine—see Section 6) when the reaction studied is the reduction of benzyl bromides with hydriodic acids ; indications of a similar phenomenon are apparent in the work of Franzen and Rosenberg (*J. pr. Chem.*, 1920, *ii*, **101**, 333) on the alkaline alcoholysis of benzyl halides ; and Tasman has shown (*Rec. trav. chim.*, 1927, **46**, 653) that the effect of different nuclear substituents on the velocity of alkaline hydrolysis of phthalides runs antiparallel to their influence on reactivity in the side-chain transformations mentioned in the preceding paragraph. A further clear illustration is available in the work of Conant, Kirner and Hussey (*J. Amer. Chem. Soc.*, 1925, **47**, 448), and especially in that of Bennett and Berry (*J. Chem. Soc.*, 1927, 1676) on the conversion of benzyl chlorides into corresponding iodides. Obviously the two groups of side-chain reactions are in some fundamental respect the inverse of each other, and this circumstance is of course, at the basis of the successful application by Lapworth and Shoesmith of the principles of alternate polarities to most of the examples studied by them.

2. *Classification of Side-chain Reactions.*

The view here under development incorporates the above analogies and conclusions, and starts from the classification of side-chain transformations given by Ingold and Rothstein (*Ann. Reports, Chem. Soc.*, 1927, **24**, 155 ; *J. Chem. Soc.*, 1928, 1217). These reactions are divided into two main categories according to whether (type A) an *influx* of electrons from the nucleus towards the side-chain, or (type B) a *recession* of electrons from the side-chain towards the nucleus, facilitates the change. The influx of electrons which assists reactions of type A may be required either to liberate or partly liberate a portion of the side-chain which carries all its electrons with it (type A_1) or to attract towards the side-chain an electron-seeking reagent (type A_2). Similarly, the electron-recession which facilitates reactions of type B may assist either the partial or complete liberation of a group which abandons a previously shared electron-pair (type B_1), or the electrostriction of a basic (positive-centre-seeking) reagent (type B_2). The following table contains some examples,

Type.	*Example.*	*Facilitated process.*
A_1	Thermal fission of benzylammonium hydroxides...	$Ph\rightarrow CH_2\text{—}\overset{\frown}{N}R_3\oplus$
,,	Acid hydrolysis of benzyl chloride	$Ph\rightarrow CH_2\text{—}\overset{\frown}{Cl}$
,,	Addition of H_2S to benzonitrile	$Ph\rightarrow C\equiv \overset{\frown}{N}$
A_2	Side-chain bromination of toluene	$Ph\rightarrow CH_2\ldots\overset{\delta+\ \delta-}{Br.Br}$
B_1	Reduction of benzyl bromide by HI	$Ph\leftarrow\overset{\curvearrowleft}{C}H_2\text{—}Br\ldots I.H$
B_2	Alkaline alcoholysis of benzyl chloride ...	$Ph\leftarrow CH_2Cl\ldots\ldots\overset{\ominus}{O}Et$
,,	Conversion of benzyl chloride into iodide ...	$Ph\leftarrow CH_2Cl\ldots\ldots\overset{\ominus}{I}$

It should be stated that, in the absence of data relating to the influence of nuclear substitution of velocity, the preliminary assignment of a side-chain reaction to its proper class is one of the main practical difficulties in the application of the theory, and that although an analysis of the circumstances of the reaction and of the type of reactivity normally characteristic of the aromatic compound and reagent is always valuable as a guide, it frequently fails to do more than indicate a probable allocation. In general, two separate points require consideration: first, a decision is required between two alternative possible machanisms, which are usually related much as are those of the second and sixth of the above examples; secondly, it must be decided which phase of the actual mechanism controls the speed, although naturally, if intermediate forms are not present in appreciable concentration, the rate-controlling phase is necessarily the initial one. The utility in connection with this part of the problem, of data relating to the influence of nuclear substitution on side-chain reactivity can immediately be made apparent without reference to the less superficial points which arise in the adaptation of the theory of nuclear aromatic substitution to side-chain reactions. Facilitation by a uniquely electron-repelling group (*e. g.*, *p*-Me) and retardation by a uniquely electron-attracting group (*e. g.*, *p*-NO_2) is diagnostic of reactions of type A, whilst the inverse of these effects characterises reactions of type B. Furthermore, it is possible to detect complications due to simultaneous membership of both types,—a condition which may arise from two

main causes: either the side-chain reaction may proceed by two contemporaneous mechanisms, one belonging to each type, or its single route may involve two rate-affecting phases, one of each type. If there are two simultaneous reactions the speeds corresponding with a series of nuclear substituents taken in order of decreasing electron-release and increasing electron-restraint should pass through a single minimum, because at both extremes of the series the acceleration of one mechanism will mask the retardation of the other ; possible examples of this effect are provided by Franzen and Rosenberg's experiments and by Berger and Olivier's investigation of the hydrolysis of benzoyl chlorides (*Rec. trav. chim.*, 1927, **46**, 516 ; compare *Ann. Reports, Chem. Soc.*, 1927, **24**, 157). If a single mechanism requires both electron-absorption and release, the velocities should pass through a single maximum, since at both ends of the series the retardation of one phase will mask the acceleration of the other ; it has been suggested (*Ann. Reports, Chem. Soc.* 1928, **25**, 147), on the basis of Lapworth and Manske's investigations (*J. Chem. Soc.*, 1928, 2533) that such conditions obtain in the formation of cyanohydrins from benzaldehydes. The matter is considered further in Section 7.

3. *Reactions Requiring Electron-release.*

A transformation having been assigned to type A, the modern theory of ordinary nuclear benzene substitution (for summary see *Rec. trav. chim.*, 1929, **48**, 799), in which it is implicit that the substituting agents require available electrons at the focus of reaction, may be applied. Adaptation is necessary, however, in order to allow for the circumstance that the effects of nuclear substituents have to traverse not only the nucleus, but also part of the side-chain in order to reach the region of reaction. It may be recalled that Ingold and Shaw (*J. Chem. Soc.*, 1927, 2918) have shown how the electron-availability at a nuclear carbon atom in a monosubstituted benzene is modified by (*a*) the nature, and (*b*) the orientation, of the substituent. As to (*a*),—groups were divided into four categories according to their electron-affinities relatively to that of the hydrogen atom they replace, and according to whether or not the groups possess unshared valency electrons, the presence of which would enable negative charges to appear in the nucleus as a result of tautomeric transformation. As to (*b*),—it was found, when the

mode of propagation of effects originating in these causes was considered, that whereas the permanent electron-affinity of the group increases or decreases the electron-availability of the *o*- and *p*-carbon atom strongly, and affects the *m*-carbon atoms in the same sense but to a smaller extent (inductive effect, $\pm I$), the existence of a mechanism whereby an electromeric charge-transfer can occur when stimulated by an electron-demanding reagent augments the effective electron-availability of the *o*- and *p*-carbon atoms, but is without sensible effect on the *m*-carbon atoms (tautomeric effect, $+T$). The following table of examples is intended to facilitate the application of these principles. The special modification which it is necessary to introduce in applying them to side-chain reactions of type A are two-fold. First, owing to the small displaceability of the electrons in a single linking, selectively heavy damping accompanies the transmission of the tautomeric effect through side-chain single-linkings to the point of reaction (compare Goss, Ingold and Wilson, *J. Chem. Soc.*, 1926, 2443; also *Rec. trav. chim.*, 1929, **48**, 804). Secondly, for a reason explained below, the tautomeric effects should, with additional damping in the nucleus, affect reactivity in *m*-side-chains.

Classification A *of Nuclear Substituents.*

($+I$, *op*-$>$*m*-activation. $-I$, *op*-$>$*m*-de-activation. $+T$, *op*-activation).

Group No.	*Mechanism.*	*Examples.*
1.	$+I$	·Me, ·CMe_3
2.	$-I$	·CO_2H, ·COMe, ·SO_2R, ·NO_2, ·$\overset{\oplus}{N}Me_3$
3.	$-I+T$	·OMe, ·Hals, ·NO, ·SOR, ·$\overset{\oplus}{S}Me_2$, ·$\overset{\oplus}{I}Ph$
4.	$-I-T$	·CR:CR′R″, ·$\overset{\ominus}{O}$

A comprehensive exemplification of this part of the general theory, which, it will be seen, incorporates the equivalent of Olivier's correlation principle, can be found in the work of Olivier, Berger, Kindler, Lapworth, Shoesmith and others already referred to (Section 1), and detailed allusion may be omitted. Further consideration may, however, appropriately be given to the two special circumstances (above) which complicate the analogy between nuclear and side-chain reactivity, since these determine the limitations affecting

the validity of Olivier's correlation principle within the field to which it was intended to apply.

4. *Limitations of the Correlation Principle.*

The effect of selective damping in the side-chain may first be considered. In group 3 of the above classification of substituents, the inductive and tautomeric effects work in opposite directions, and everything depends, therefore, on the relative importance, so far at least as concerns *op*-nuclear reactivity and type-A reactivity in *op*-side-chains. The inductive effect results in de-activation, to an extent depending on the electron-affinity of the group; the tautomeric effect leads to activation, in proportion to the tendency of the unshared electrons to become shared, that is, to the basicity of the group. Now the electron-affinity of the halogens in the neutral state is pronounced (compare stability of the halide ions), but iodine differs from the others in possessing considerable basicity (compare stability of iodinium ions); and in nuclear substitution (nitration) it has been found (Ingold and Shaw, *loc. cit.*) that, for iodine, the tautomeric effect predominates, this element belonging to the *op*-activating section of the group-3 substituents, whilst, for the other halogens, the inductive effect has main importance, and these belong to the de-activating series. In type-A side-chain reactions, on the other hand, the tautomeric effect of iodine, presumably owing to selective damping, no longer outweighs the inductive, and this element ranges itself with the other halogens as a de-activating substituent. It will be seen that the iodine substituent qualitatively violates Olivier's correlation principle, and that the broader theory naturally accommodates the apparent anomaly.

Before exemplifying tautomeric polar influence on reactivity in a *m*-side-chain, a few words of explanation are desirable with regard to the theoretical inference that such effects should be perceptible. It will be readily understood how, in nuclear substitution, in which the reagent normally has the choice of exciting and thereafter utilising, the tautomeric effect in those positions (*o*- and *p*-) in which they are primarily, and hence most easily, stimulated, the orientation process is largely self-definitive,—the reagent becoming more and more irrevocably committed to *o*- or *p*-attack during its approach, from the moment when it began to exert electrical action on the aromatic molecule until union is definitely accomplished; thus it is that the

$+T$-effect (unlike the $+I$-effect which is a permanent property of the aromatic molecule) never leads to appreciable *m*-substitution. On the other hand, a reagent attacking a *m*-side-chain has no alternative method of utilising an existing mechanism for tautomeric electron displacement within the nucleus than that of allowing the final stages of transmission of the effect of such displacements to proceed to the point of reaction by ordinary induction; and thus a substituent should, by its tautomeric, as well as by its inductive, effect, influence reactivity in *m*-side-chains, although naturally to a less degree than were the side-chains otherwise situated. It is possible to perceive the operation of this principle in several recorded observations on side-chain reactions, but all are rendered more or less complicated by the simultaneous presence of the inductive effect, the relay of which to the *m*-position is not peculiar to side-chain reactions. In the experimental part of this paper, however, we show that a *m*-phenyl substituent appreciably increases the speed of acid hydrolysis of benzyl bromide. Now phenyl (a form of substituted vinyl) is a substituent of group 4 in the above classification, but its inductive effect is negligibly small; in diphenyl itself it is not merely small, but is zero, both from symmetry and from the determined zero dipole moment of this hydrocarbon. The strong *op*-orienting action of phenyl is, of course, a manifestation of its tautomeric effect. Therefore, since in the phenyl-substituted benzyl bromide the tautomeric effect alone is under observation, the experiments referred to definitely confirm the anticipated cause of failure here considered of the simple analogy with nuclear substitution.

5. *Reactions Requiring Electron-restraint.*

For side-chain reactions known to belong to type B, the procedure corresponding to that described above, utilises, not the analogy of ordinary nuclear substitution, that is, the replacement of nuclear hydrogen by the action of negative-centre-seeking reagents, but the analogy furnished by aromatic substitution reactions in which the replacement of electro-negative elements such as chlorine is effected by the attack of positive-centre-seeking (basic) reagents. The theory of this kind of aromatic substitution has not yet been greatly developed, but it has been outlined (Ingold, *Rec. trav. chim.*, 1929, **48**, 809); and the main features are, first, that the manifestations of the

inductive effect become reversed in sign, $+I$ representing de-activation and $-I$, activation, although their nuclear distribution, $op > m$, remains as before ; and second, that whilst the tautomeric effect $+T$ is not stimulated by the reagents now under consideration an *op*-activating tautomeric effect $-T$, depending on $\alpha\beta$-unsaturation in the orienting substituent, is rendered operative by such reagents, since this structural feature permits the appearance in the nucleus of positive charges by electromeric transfer. This scheme of classification, which is illustrated in the table below, will also apply to side-chain reactions of type B, after introduction of qualifications, similar to those mentioned in section 3, relating to the diminished relative importance of the tautomeric effect, and the ability of this effect to penetrate a *m*-side-chain.

Classification B *of Nuclear Substituents.*

($+I$, $op- > m$-de-activating. $+I$, $op- > m$-activating. $-T$, *op*-activating.)

Group No.	*Mechanism.*	*Examples.*
1.	$+I \rangle \leftarrow R$	Me, CMe_3, $\overset{\ominus}{O}$
2.	$-I \rangle \rightarrow R$	Hals., $\overset{\oplus}{N}Me_3$
3.	$-I-T \rangle \overset{\curvearrowright}{\leftarrow} R$	CO_2H, NO, NO_2, CN.
4.	$+I-T \rangle \overset{\curvearrowright}{\rightarrow} R$	$CR{:}CR'R''$.

On comparing this scheme with that mentioned in Section 3, it becomes evident that, owing to the radically altered nature of the tautomeric effect, the influence of groups on the kind of nuclear substitution now considered is far from being uniformly the inverse of their influence on reactivity in the replacement of nuclear hydrogen. On the other hand, in side-chain transformations, the diminished importance of the tautomeric effect leads to a certain simplification of the theory, inasmuch as it renders the modifying influence of groups on type-B reactivity more nearly the uniform inverse of their effect on reactivity in changes of type-A. In short, a fairly consistent inversion of the kind indicated is to be expected, and it is on this basis that the theory accommodates the series of relations formerly elucidated by the principle of alternate polarities. Ample illustration of this matter is to be found in the

work of Oliver, Tasman, Lapworth, Shoesmith, Conant, Bennett and others already mentioned (Section 1); at the present stage more nt erest attaches to expected departures from exact inversion. This is discussed in the next Section, but it is appropriate to mention here that the appended experimental record contains a proof, on similar lines to those indicated in Section 4, that the kind of tautomeric effect which is specially characteristic of side-chain reaction of type B, *can* influence reactivity in a *m*-side-chain.

6. *Limitations of the Inversion Principle.*

Failure of the inversion rule is to be expected amongst groups which are associated with a powerful tautomeric (or weak inductive) effect, and at the same time fulfil one of two conditions relating to classification. These conditions are (1) that the group shall belong to group 3 of classification A and also to either of groups 2 or 3 of classification B, and (2) that it shall belong to either of groups 1 or 4 of the A-classification, and also to group 4 of the B-classification.

An illustration is furnished by the anomalous behaviour of chlorine and bromine mentioned in Section 1. These substituents fulfil the first of the above alternative classificatory conditions since they belong to group 3 of the type-A scheme, and group 2 of the type-B scheme. In nuclear substitution they are in the peculiar position of being de-activating but *op*-orienting; that is, their inductive effect ($-I$) depresses reactivity throughout the nucleus, the *m*-positions included, whilst their tautomeric effect ($+T$) restores activity to the *op*-positions only, raising them above the standard of reactivity set by the de-activated *m*-position (*op*-orientation) but not up to the standard represented by unsubstituted benzene (de-activation). In the acid hydrolysis of the chloro- and bromo-benzyl bromides (type-A reaction) these phenomena qualitatively repeat themselves: the substituted compounds are all hydrolysed more slowly than benzyl bromide, but the isomerides amongst themselves stand in the order $op > m$ as regards their rates of reaction. Turning to the reduction of these compounds (type-B reaction), the tautomeric effect ($+T$) of the nuclear substituents should be inoperative and their inductive effect ($-I$) should activate in all positions in the normal order, $op > m$; and this is what happens. In short, when the substituted compounds are compared with the unsubstitued parent the inversion rule holds, but when the substituted

isomerides are compared amongst themselves the inversion rule fails. The anomaly, although inconsistent with any simple alternating principle, is thus naturally accommodated by the view here developed.

In the appended experimental record will be found an instance illustrating the even more complete failure of the inversion principle. The nuclear substituent was chosen to fulfil the second of the two alternative classificatory conditions, and in selecting i twe had in mind, not only the further theoretical requirement that its inductive effect should be relatively small, but also the practical one that it should be inert towards the reagents employed. The latter condition ruled out many forms of the substituted vinyl group which otherwise would have been suitable. On the other hand, phenyl is a group which possesses the necessary stability and has the added advantage that its inductive effect is entirely negligible. The influence of the nuclear phenyl substituent on certain side-chain transformations was therefore investigated, and following precedent, we utilised the acid hydrolysis of benzyl bromides as representative of side-chain reactions of type-A, whilst reduction of the same compounds with hydriodic acid served to exemplify the reactions of type-B. We are able to show, first that the introduction of a phenyl group into either the *m*- or *p*-position of benzyl bromide enhances both the velocity of hydrolysis and that of reduction, and secondly, that, as regards the relative reactivities of isomerides, the *m*- and *p*-compounds retain the same order, namely $p>m$, for both reactions. The inversion principle thus fails on both counts, and it is clear that, as theoretically anticipated, whilst the phenyl group has the ability to generate tautomeric electron-displacements in either sense, the direction of the displacements actually stimulated in a given case depend on the necessities of the attacking reagent. Incidentally it may be noted that this is exactly the result which is needed to reconcile the observed effects of phenyl in another field of investigation, in which it has found that this group can excite mobility in attached tautomeric systems, not only when the displaceable atom is released as a cation (*e.g.*, H,-"prototropy") but also when it migrates as an anion (*e.g.* Br,-"anionotropy"); these observations necessitate the assumption of electron-absorption or-release by phenyl according to the electrical requirements of the kind of tautomerism involved (Burton, Ingold and Shoppee, *J. Chem. Soc.*, 1928, 904, 1650; 1929, 447, 1199).

7. *Reactions Requiring Electron-absorption and Release.*

It is necessary to refer once more to the classification of side-chain reactions which forms the starting point of the considerations here presented. The classification assumed that side-chain reactions depend on a preliminary dissociation or association, in the course of which an electric charge, appearing in the side-chain, leads to consequential electrical adjustments as between the side-chain, the nucleus and any substituents attached thereto. When several aromatic nuclei possess a common side-chain a counterpart to these assumed, transient dissociations can be found in directly demonstrable ionic equilibria in which the charged components have considerable life (*e.g.*, $Ph_3C{\cdot}K$ and $Ph_3C{\cdot}Cl$ in ionising solvents) ; but, under the same structural conditions, another type of dissociation also becomes directly observable, in which the separable components apparently bear no charge (*i.e.*, $Ph_6C_2 \rightleftharpoons 2Ph_3C$ in non-ionising solvents). A theory of side-chain reactivity obviously cannot be general unless it includes recognition of this type of dissociation also, not only when it is pronounced as in the chemistry of free radicals, but also in any of its more ephemeral manifestations, should these arise in other circumstances. The conditions leading to the stability of free radicals have been considered by Burton and Ingold (*Proc. Leeds Phil. Soc.*, 1929, **1**, 421) whose conclusions, in so far as they affect the question under discussion, may be summarised as follows: The side-chain of a free radical, although neutral, may be regarded as initially unsaturated, with respect to both negative and positive electricity, because it requires to gain or lose an electron in order to complete its duplets (achieve spin-symmetry), and to lose or gain an electronic charge in order to recover the neutrality which the completion of the duplets would destroy. Now if this interpretation of the electrostatic condition of free radicals is correct, then the essential condition for promoting dissociation into neutral components is the possibility of *duplex* electrical re-adjustments ; and if this actually is the case, a general provision for side-chain reactions depending on such a mechanism has already been made (although not hitherto explicitly) in the foregoing statement of the theory, inasmuch as reactions have been envisaged which are characterised by the inclusion within a single mechanism of " phases " (which need not necessarily be *stages* in the sense implying separation in time) respectively

dependent on electron-absorption and release. Some justification for contemplating such a category of side-reactions is to be found in the fact that the inferred practical criterion relating to the effect of nuclear substituents has been experimentally encountered (Section 2) but the investigation referred to did not include a study of the phenyl substituent, the duplex tautomeric effect of which should place it in a highly peculiar position with respect to such reactions. In this conclusion one may perceive a reason why the sufficient accumulation of phenyl, or other aryl groups possessing a common side-chain constitutes almost the only known structural condition for the realisation of considerable dissociation into neutral components; furthermore the obvious corollary that the introduction of phenyl substituents into any positions (but especially into the *o*- or *p*-positions) of the aromatic nuclei bearing the side-chain should increase such dissociation is confirmed, so far as substitution in the *p*-position is concerned by Schlenk's well-known work on free radicals containing the *p*-diphenylyl group. Apart from the *p*-diphenylyl, however, other polynuclear aryl groups are known markedly to facilitate dissociation into radicals, and since the order of the relative intensities with which they do so is also known, a simple test of the whole matter can be made.

The work of Schlenk and Gomberg and their collaborators (*Annalen*, 1910, **372**, 1 ; *J. Amer. Chem. Soc.*, 1917, **39**, 1652 ; 1922, **44**, 1829) establishes the sequence—

α-naphthyl>β-naphthyl>*p*-diphenylyl>phenyl

for the ability of these groups to promote dissociation into neutral radicals. If this sequence is to be interpreted as representing capacity for the duplex electrical readjustments reffered to above, then the same series should represent in addition, firstly, the order in which the groups facilitate side-chain reactions involving dissociations dependent on electron-release (reactions of sub-type A_1), and secondly, the relative facilitation by the groups of side-chain transformations dependent on dissociations demanding electron-restraint (reactions of sub-type B_1). The reactions we have studied belong respectively to these sub-types; and for both reactions we find a sequence identical with the above:

α-naphthyl>β-naphthyl>*p*-diphenylyl>*m*-diphenylyl>phenyl.

It is scarcely necessary to add that completeness is not claimed

for theoretical treatment here outlined. In particular, separate discussion is required regarding two other structural influences, namely, those due to external molecular electric fields, and to steric factors, which become of considerable importance in certain cases of *o*-substitution.

Experimental.

1. *Preparation of Aryl Methyl Bromides.*

3-*Bromomethyldiphenyl.*—3-Methyldiphenyl was prepared by a method identical in principle with that of Perrier (*Bull. Soc. Chim.*, 1892, [3], **7**, 181) and purified by alternate fractionation (column) and freezing. Bromination was effected by leading dry bromine (10% excess) into the hydrocarbon at 200° (bath temperature) and fractionating the product. The pale yellow oil, b.p. 150°/15 mm., consisted essentially of 3-bromomethyldiphenyl contaminated by an inert impurity not containing side-chain bromine. Therefore, as preliminary to the quantitative work described below, the percentage purity of each sample was determined by treatment with alcoholic trimethylamine and estimation of the ionic bromine thus formed. m-*Phenylbenzyltrimethylammonium picrate*, obtained by addition of aqueous sodium picrate to a solution of the quaternary ammonium bromide prepared in this way, separated from aqueous alchohol in rhombic plates, m.p. 152°. (Found: C, 58·2; H, 4·79. $C_{22}H_{22}O_7N_4$ requires C, 58·15; H, 4·85 per cent.).

4-*Bromomethyldiphenyl.*—4-Methyldiphenyl was prepared (compare Carnelly, *J. Chem. Soc.*, 1876, **29**, 13), purified, and brominated as in the former example, and the bromination product fractionated. The portion, b.p. 130-140°/10 mm., which solidified on cooling, yielded 4-*bromomethyldiphenyl* as pearly leaflets, m.p. 82°, on crystallising from a mixture of ether and ligroin below 0°. (Found: C, 63·3; H, 4·36. $C_{13}H_{11}Br$ requires C, 63·2; H, 4·45 per cent.). The substance gave the theoretical proportion of bromide ion when treated with trimethylamine by the method illustrated for the *m*-compound and the quaternary ammonium bromide solution, when treated with aqueous sodium picrate, yielded p-*phenylbenzyltrimethyammonium picrate*, which crystallised from aqueous alcohol, in rhombic plates, m.p. 179°. (Found: C, 57·9; H, 5·11.

$C_{22}H_{22}O_7N_4$ requires C, 58·15; H, 4·85 per cent.). The less volatile portion of the bromination product on crystallisation from alcohol, with use of charcoal, yielded a yellow microcrystalline powder, m.p. 129°. Analysis showed this to be a *dibromo-4-methyldiphenyl*. (Found: C, 48·0 ; H, 3·32. $C_{13}H_{10}Br_2$ requires C, 48·1 ; H, 3·07 per cent.). Except that its stability to boiling alcohol indicates that both bromine atoms are attached to the nucleus, there is no evidence of their orientation, but the most probable positions would appear to be the 2:4′-positions.

α-Bromomethylnaphthalene.—This was prepared as described by Schmidlin and Massini (*Ber.*, 1909, **42**, 2389), but we confirm Shoesmith and Rubli's statement (*J. Chem. Soc.*, 1927, 3098) that it is a crystalline solid, m.p. 53°.

β-Bromomethylnaphthalene.— The compound, which had the properties recorded by Schultz (*Ber.*, 1884, **17**, 1529), was prepared by his method, except that the temperature during bromination was maintained at 200°.

2. *Hydrolysis of Aryl Methyl Bromides.*

General method.—Weighed quantities (about 0·08 g.) of the bromide, each dissolved in 100 c.c. of 90% aqueous alcohol, were kept in a thermostat at 24° for various measured periods of time and the liberated hydrobromic acid titrated with carbonate-free sodium hydroxide. Usually from 20-45% of the complete reaction was followed in this way, and the velocity coefficients were then calculated from each observation by means of the formula $k=(1/t) \times \log_{10} a/(a-x)$, the units of time being minutes.

Preliminary experiments with β-bromomethylnaphthalene in which the reaction was followed nearly to completion showed that its course substantially conforms to the unimolecular law although the calculated coefficients tends to fall slightly near the end of the process.

Results.—These are summarised in the following table, in which the second set of determinations relating to β-bromomethylnaphthalene is included to show that the disturbance associated with the " tail " of the reaction is without influence on the velocity coefficients recorded for the first 20-45% of hydrolysis, since, even

if as much as 80% of the change is followed, the mean coefficient remains substantially the same:—

Substance hydrolysed.	Number of observations.	Percentage of reaction followed.	Calc. $k \times 10^6$		
			Minimum.	Maximum.	Mean.
Benzyl bromide	3	20·7	76	79	78
3-Bromomethyldiphenyl.	6	34·3	138	154	146
4-Bromomethyldiphenyl.	8	37·5	158	173	165
β-Bromomethylnaphthalene.	5	45·3	170	192	184
,,	10	81·5	177	195	185
α-Bromomethylnaphthalene.	6	40·7	203	227	220

The relative values of the coefficients obtained for α- and β-bromomethylnaphthalene are consistent with Shoesmith and Rubli's observations on these substances (*loc. cit.*).

3 *Reduction of Aryl Methyl Bromides.*

General Method.—(*a*) Weighed quantities of each bromide (about 0·15 g.) were reduced for 1 or 2 hours at 100° in 10 c.c. of a solution prepared from constant-boiling hydriodic acid (1 vol.) and glacial acetic acid (10 vols.), and the liberated iodine estimated as usual. Simultaneously with each experiment a control was perfomed in which all conditions were maintained the same, except for the omission of the bromide, the object being to eliminate error arising from the liberation of iodine by atmospheric attack.

(*b*) Weighed quantities (about 0·3 g.) of those bromides which were found to be reduced nearly completely under the conditions of method (*a*) were each reduced at 66° for 6 or 15 hours with 10 c.c. of a solution prepared by making 1 vol. of constant-boiling hydriodic acid up to 5 vols. with glacial acetic acid. The remainder of the experiment, and the controls, were carried out as above.

Results.—These are recorded in the following table, the footnote to which illustrates the degree of consistancy of individual experiments.

Substance reduced.	Percentage reduction.			
	Method (*a*)		Method (*b*)	
	1 hour.	2 hours.	6 hours.	15 hours.
Benzyl bromide	—	32*	—	—
3-Bromomethyl-diphenyl.	26	43	—	—
4-Bromomethyl-diphenyl	36	67	—	—
β-Bromomethyl-naphthalene.	95	99	23	41
α-Bromomethyl naphthalene.	96	99	35	50

* (Individual values : 32, 34, 30, 30·5 %).

The results for the bromomethylnaphthalenes are not in good agreement with those obtained by Shoesmith and Rubli (*loc. cit.*).

Summary.

A theory of aromatic side-chain reactivity, linking this subject on the one hand with nuclear aromatic substitution and on the other with pure radical chemistry, is advanced and supported by observations on the reactivity in hydrogen and reduction of polynuclear analogoues of benzyl bromide.

One of us (C. S. P.) desires here to acknowledge his indebtedness to the Government of H. H. the Maharaja Gaekwar of Baroda for granting to him a period of study-leave during which this investigation has been carried out.

The University, Leeds.

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Interaction of Chlorosulphonic Acid with the Substituted Amides of Malonic and Methylmalonic Acids.

By K. G. Naik and C. H. Shah.

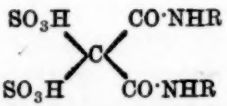
The investigation which forms the subject of this communication was undertaken with a view to study the reactivity of the two hydrogen atoms of a reactive methylene group situated between two carbonyl groups, $-CO\cdot CH_2\cdot CO-$, as in the case of the substituted amides of malonic acid. Reference is invited to a previous communication by Naik and Amin (*J. Indian Chem. Soc.*, 1928, **5**, 579). Attention is here confined to the study of the interaction of some of the substituted amides of malonic acid using chlorosulphonic acid as the reagent. For this purpose the interaction of chlorosulphonic acid with the following substances was studied:—

(1) Malon-diphenylamide, (2) Malon-dibenzylamide, (3) Malon-di-*p*-tolylamide, (4) Malon-di-*o*-tolylamide, (5) Malon-di-*m*-tolylamide, (6) Malon-di-α-naphthylamide, (7) Malon-di-β-naphthylamide, (8) Malon-di-(1:3:4)-xylidide, (9) Malon-dipropylamide, (10) Malon-mono-*p*-tolylamide, (11) Methylmalon-diphenylamide, (12) Methylmalon-di-*p*-tolylamide, (13) Methylmalon-di-*o*-tolylamide, (14) Methylmalon-di-*m*-tolylamide, (15) Methylmalon-di-α-naphthylamide, (16) Methylmalon-di-β-naphthylamide, (17) Methylmalon-di-(1:3:4)-xylidide.

Of the above, compounds, 8, 15, 16 and 17 were prepared for the first time, by the same method as that used for preparing the corresponding amides of malonic acid.

The results of the present investigation could be summarised as under:—

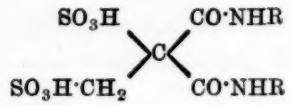
Type I. Compounds (1) to (10), with the exception of (9), react to form disulpho-compounds whose constitution can be generally represented as:—



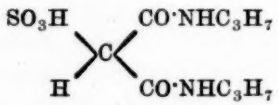
(I)

(R=phenyl, benzyl, tolyl, naphthyl, or xylyl group.)

Type II. Compounds (11) to (17) give rise to disulpho-derivatives, which can generally be represented as:—



Compound (9) reacts with chlorosulphonic acid to form a derivative which can be represented as:—



That the constitution assigned to (I, R = Ph) is correct and that all the sulpho-acids, derived from the various amides enumerated above, can generally be thus represented, follows from the following considerations:—

(*i*) That the hydrogen atoms attacked by the chlorosulphonic acid are not eliminated from the phenyl groups or any such analogous nucleus becomes evident from the course of the reaction in the case of malon-dipropylamide where no such aromatic nuclei are present, and yet the sulpho-acid is produced.

(*ii*) That the hydrogen atoms eliminated were not those which were originally attached to the two nitrogen atoms, because only one sulpho-group enters in malon-dipropylamide, though there are two symmetrically situated $-NH-$ groups present in it.

The compounds enumerated under type (I) reacted similarly with chlorosulphonic acid. Only in the case of malon-di-α-naphthylamide, a longer time was required before the reaction was complete.

In the above cases, molecular proportions of the reacting substances did not give a good yield of the sulpho-acids and much of the amide remained unaltered. When they were taken in equal quantities, the yield improved and the products were obtained in a purer state.

With a view to study the stability of the two sulphonic acid groups, attached to the methylene carbon atom, it was thought desirable to see how far these groups could be replaced by a negative group, such as the nitro-group.

The following four compounds were, therefore, subjected to a process of nitration:—

(1) Disulpho-malon-diphenylamide;
(2) Disulpho-malon-di-*p*-tolylamide;
(3) Disulpho-malon-di-*o*-tolylamide;
(4) Sulphomethyl-sulphomalon-diphenylamide.

Compounds (2) and (3) when treated with dilute nitric acid yielded dinitro-derivatives, thus:—

$$(HSO_3)_2:C:(CO\cdot NHC_7H_7)_2 \xrightarrow{HNO_3} (NO_2)_2:C:(CO\cdot NHC_7H_7)_2.$$
$o-$ and $p-$

Compounds (1) and (4) on being nitrated gave tetranitro-derivatives. Thus in the case of (1) the reaction followed the course as under:—

$$(HSO_3)_2:C:(CO\cdot NHC_6H_5)_2 \xrightarrow{HNO_3} (NO_2)_2:C:(CO\cdot NHC_6H_4NO_2)_2.$$

The tetranitro-derivative obtained from disulpho-malon-diphenylamide was hydrolysed with 50 per cent. aqueous caustic potash solution, thus:—

$$(NO_2)_2:C:(CO\cdot NHC_6H_4\cdot NO_2)_2 + 2KOH = (NO_2)_2:C:(CO_2K) + 2C_6H_4(NH_2)NO_2.$$

The formation of potassium dinitro-malonate as above shows that the two $-SO_3H$ groups originally present in the disulpho-amide, were replaced by the nitro-groups, the other two being present in the aromatic nuclei of the above amide. Both the sulpho-groups seem to have been simultaneously replaced by the two nitro-groups.

Experimental.

A general method of preparing the sulpho-acids is to add equal quantities of the amide and chlorosulphonic acid to dry chloroform in a conical flask. When properly mixed the reaction starts and proceeds vigorously with much evolution of heat. Clouds of hydrogen chloride are thrown out in the initial stage of the reaction. The flask is kept normally cool by holding under a water-tap. Subsequently, the mixture is refluxed on a sand-bath for two hours, when

the evolution of hydrogen chloride stops. The solvent is then removed and the red syrupy reaction product poured into 100 c.c. of water. The syrupy mass goes into solution. On concentration and cooling, the sulpho-acid separates out in clusters of shining leaflets.

Disulpho-malon-diphenylamide.—It was obtained from malondiphenylamide (3 g.) and chlorosulphonic acid (3 g.) in 20 c.c. of chloroform. It formed shining colourless leaflets, soluble in water, and insoluble in alcohol, acetone, acetic acid, benzene, toluene, carbon disulphide, carbon tetrachloride, ether, ethyl acetate, nitrobenzene and light petroleum. It has no definite m.p. but decomposes above 280°. It crystallises out with two molecules of water of crystallisation, which is lost when heated to 140–150° for four hours. (Found: S, 14·3; H_2O, 7·6; Equiv. wt., 224. $C_{15}H_{14}O_8N_2S_2,2H_2O$ requires S, 14·2; H_2O, 8·0 per cent. Equiv. wt., 225).

Nitration.—The above disulpho-acid (2 g.) was gradually added to a mixture of 20 c.c. of nitric acid (*d* 1·2) and 20 c.c. of glacial acetic acid. On warming the mixture, oxides of nitrogen began to evolve. The reaction mixture was kept on a water-bath till the evolution of the fumes ceased. Then the remaining fumes of nitrogen peroxide were blown away by air and the mixture poured into water. On concentration, the nitro-compound crystallised out in the form of deep orange crystals, m. p. 124°. The product was found to be soluble in alcohol, benzene, chloroform, acetone and nitrobenzene. (Found: N, 19·32. $C_{15}H_{10}O_{10}N_6$ requires N, 19·35 per cent.).

Hydrolysis of Dinitromalon-dinitrodiphenylamide.—About 2 g. of the substance were refluxed for several hours with 50 per cent. caustic potash solution and the resulting solution was filtered. The filtrate was concentrated on the water-bath, when potassium dinitromalonate separated out, which was collected, and recrystallised from hot water. (Found: K, 29·02. $C_3O_8N_2K_2$ requires K, 28·88 per cent.).

The *barium salt*, $Ba(SO_3)_2:C:(CO{\cdot}NHC_6H_5)_2,H_2O$, was prepared by digesting an aqueous solution of the acid with barium carbonate. The solution was filtered and the filtrate on being concentrated deposited the barium salt as needle-shaped crystals. (Found: H_2O, 3·09; Ba, 24·41. $C_{15}H_{12}O_8N_2S_2Ba,H_2O$ requires H_2O, 3·17; Ba, 24·2 per cent.).

The *potassium salt*, $(KSO_3)_2:C:(CO{\cdot}NHC_6H_5)_2,9H_2O$, was prepared by the action of caustic potash on the solution of the acid.

(Found: H_2O, 24·46; K, 11·94. $C_{15}H_{12}O_8N_2S_2K_2,9H_2O$ requires H_2O, 24·85; K, 11·96 per cent.).

The *sodium salt*, $(NaSO_3)_2:C:(CO\cdot NHC_6H_5)_2,3H_2O$, was prepared in a similar way using caustic soda. (Found: H_2O, 10·33; Na, 9·01. $C_{15}H_{12}O_8N_2S_2Na_2,3H_2O$ requires H_2O, 10·54; Na, 8·98 per cent.).

Calcium salt.—It was prepared like the barium salt, and crystallised from alcohol. (Found: Ca, 8·5. $C_{15}H_{12}O_8N_2S_2Ca$, H_2O requires Ca, 8·51 per cent.).

Ammonium salt.—The solution of the acid was just neutralised with ammonium hydroxide and concentrated when it crystallised out in large prisms. (Found: H_2O, 3·84; N, 12·06. $C_{15}H_{20}O_8N_4S_2$, H_2O requires H_2O, 3·86; N, 12·01 per cent.).

Disulphomalon-dibenzylamide.—Two g. of the amide were made to react with 2 g. of the acid in 20 c.c. of chloroform. The reaction product was obtained by a process similar to that followed in the preparation of disulphomalon-diphenylamide. The pure substance was crystallised from distilled water. It had no definite melting point, but decomposed at temperatures above 300°. (Found: H_2O, 3·98; S, 14·08. $C_{17}H_{18}O_8N_2S_2,H_2O$ requires H_2O, 8·61; S, 13·9 per cent.).

The *barium salt*, $Ba(SO_3)_2:C:(CO\cdot NHC_7H_7)_2,\frac{1}{2}H_2O$ was prepared as usual by neutralising the sulpho-acid with barium carbonate. (Found: H_2O, 1·54; Ba, 23·43. $C_{17}H_{16}O_8N_2S_2Ba,\frac{1}{2}H_2O$ requires H_2O, 1·53; Ba, 23·42 per cent.).

Sodium salt.—It was prepared as usual. (Found: Na, 9·44. $C_{17}H_{16}O_8N_2S_2Na_2$ requires Na, 9·46 per cent.).

Potassium salt.—(Found: K, 15·12. $C_{17}H_{16}O_8N_2S_2K_2$ requires K, 15·05 per cent.).

The *ammonium salt*, $(NH_4SO_3)_2:C:(CO\cdot NHC_7H_7)_2,\frac{1}{2}H_2O$, was prepared by neutralisation of the acid with ammonium hydroxide. (Found: H_2O, 1·46; N, 11·31. $C_{17}H_{24}O_8N_4S_2,\frac{1}{2}H_2O$ requires H_2O, 1·82; N, 11·33 per cent.).

Disulphomalon-di-p-tolylamide.—The amide (3 g.) was made to react with chlorosulphonic acid (3 g.) in 25 c.c. of dry chloroform. The product (which was obtained by the method adopted in the previous cases) was found to be insoluble in all organic solvents. It was soluble only in hot water and had no definite melting point but decomposed at 300°. (Found: S, 14·42. $C_{17}H_{18}O_8N_2S_2$ requires S, 14·47 per cent.).

Hydrolysis.—The above acid (5 g.), was added to a solution of 30 g. of caustic soda in 100 c.c. of alcohol and the whole refluxed for 48 hours. The resulting product was diluted with water and then extracted with ether. The ethereal extract deposited *p*-toluidine after removal of ether.

Nitration.—The acid (1 g.) was added to 20 c.c. of dilute nitric acid. On heating and concentrating the solution, the reaction product was obtained as orange crystals very soluble in alcohol, benzene, acetone and acetic acid but sparingly so in petroleum. It melts at 68°. (Found: N, 14·08. $C_{17}H_{16}O_8N_4$ requires N, 13·86 per cent.).

Disulphomalon-di-o-tolylamide.—Two g. of the amide and 3 g. of chlorosulphonic acid were used. On crystallisation from water the product formed long, silky needles. (Found: S, 14·5. $C_{17}H_{18}O_8N_2S_2$ requires S, 14·47 per cent.).

Potassium salt.—(Found: K, 15·06. $C_{17}H_{16}O_8N_2S_2K_2$ requires K, 15·05 per cent.).

Nitration.—The acid, on nitration, as in the case of the *para*-derivative, gave a greenish coloured product, m.p. 85°. (Found: N, 15·1. $C_{17}H_{16}O_6N_4$ requires N, 15·05 per cent.).

Disulphomalon-di-m-tolylamide.—Two g. of the amide and 2 g. of the acid in 20 c.c. of chloroform were taken. The product was obtained from water in white plates. (Found: S, 13·9; H_2O, 3·93. $C_{17}H_{18}O_8N_2S_2,H_2O$ requires S, 13·9; H_2O, 3·91 per cent.).

The *calcium salt* was prepared as usual. (Found: Ca, 8·47. $C_{17}H_{16}O_8N_2S_2Ca$ requires Ca, 8·3 per cent.).

Disulphomalon-di-α-naphthylamide.—This was prepared by allowing 3 g. of the amide to react with 10 g. of the acid in 30 c.c. of chloroform. The product was found to be soluble only in water. (Found: H_2O, 12·92; S, 11·01. $C_{23}H_{18}O_8N_2S_2,4H_2O$ requires H_2O, 12·2; S, 10·92 per cent.).

Disulphomalon-di-β-naphthylamide.—Two g. of the amide were treated with 10 g. of chlorosulphonic acid. The disulpho-derivative was found to be very sparingly soluble in water. It had no definite melting point but decomposed at 280°. (Found: H_2O, 17·4; S, 10·32. $C_{23}H_{18}O_8N_2S_2,6H_2O$ requires H_2O, 17·36; S, 10·28 per cent.).

Monosulphomalon-dipropylamide.—Two g. of the amide were made to react with 2 g. of the acid. The product could not be isolated in crystalline form, but was obtained as a red syrup. It was

soluble in all organic solvents. Its *barium salt* was obtained in the form of large shining leaflets from water. (Found: H_2O, 7·5; Ba, 19·08. $C_{18}H_{34}O_{10}N_4S_2Ba,3H_2O$ requires H_2O, 7·4; Ba, 19·00 per cent.).

*Disulphomalon-mono-*p*-tolylamide*.—This was prepared by treating the mono-amide (2 g.) with chlorosulphonic acid (2 g.) in the usual manner. It was crystallised from water in short needles. (Found: H_2O, 4·93; S, 17·27. $C_{10}H_{12}O_8N_2S_2,H_2O$ requires H_2O, 4·8; S, 17·29 per cent.).

Disulphomalon-di-(1 : 3 : 4)*xylidide*.—The product from 2 g. of the xylidide and 2 g. of the sulphonic acid separated as white lustrous laminae from hot water. (Found: S, 18·62. $C_{19}H_{22}O_8N_2S_2$ requires S, 13·61 per cent.).

Sulphomethyl-sulphomalon-diphenylamide.—It was prepared by the interaction of 2 g. of the amide and 2 g. of the acid. It comes out from water in white crystals. (Found: S, 14·94. $C_{16}H_{16}O_8N_2S_2$ requires S, 14·95 per cent.).

Nitration.—The acid was gradually added to a mixture of 20 c.c. of nitric acid (*d* 1·2) and 20 c.c. of acetic acid. After the evolution of the oxides of nitrogen had ceased, it was poured in a small quantity of water, when the nitrated product came out as yellow crystals, m.p. 120°. (Found: N, 18·78. $C_{16}H_{12}O_{10}N_6$ requires N, 18·75 per cent.).

Potassium salt.—(Found: K, 14·97. $C_{16}H_{14}O_8N_2S_2K_2,H_2O$ requires K, 14·94 per cent.).

Sodium salt.—(Found: Na, 9·71. $C_{16}H_{14}O_8N_2S_2Na_2$ requires Na, 9·74 per cent.).

*Sulphomethyl-sulphomalon-di-*p*-tolylamide*.—It was obtained in the form of shining needles from hot water. (Found: H_2O, 3·9; S, 13·56. $C_{18}H_{20}O_8N_2S_2,H_2O$ requires H_2O, 3·8; S, 13·5 per cent.).

*Sulphomethyl-sulphomalon-di-*o*-tolylamide*.—It was obtained from water in white shining crystals, by a process similar to the above. (Found: H_2O, 3·92; S, 13·6. $C_{18}H_{20}O_8N_2S_2,H_2O$ requires H_2O, 3·8; S, 13·5 per cent.).

Potassium salt.—(Found: H_2O, 6·4; K, 13·71. $C_{18}H_{18}O_8N_2S_2K_2,2H_2O$ requires H_2O, 6·33; K, 13·73 per cent.).

*Sulphomethyl-sulphomalon-di-*m*-tolylamide* was prepared in the usual way, from methylmalon-di-*m*-tolylamide. (Found: S, 14·12. $C_{18}H_{20}O_8N_2S_2$ requires S, 14·03 per cent.).

Sulphomethyl-sulphomalon-di-α-naphthylamide.—It was obtained from 2 g. of the amide and 10 g. of chlorosulphonic acid. (Found: H_2O, 14·54; S, 10·37. $C_{24}H_{20}O_8N_2S_2,5H_2O$ requires H_2O, 14·56; S, 10·36 per cent.).

Sulphomethyl-sulphomalon-di-β-naphthylamide was obtained in a similar way. (Found: H_2O, 9·4; S, 11·01. $C_{24}H_{20}O_8N_2S_2$, $3H_2O$ requires H_2O, 9·28; S, 10·99 per cent.).

Sulphomethyl-sulphomalon-di-(1:3:4)*xylidide* was obtained in the form of white scales. (Found: S, 13·24. $C_{20}H_{24}O_8N_2S_2$ requires S, 13·22 per cent.).

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Studies on Hexammine Cobaltic Sulphate. Part I.

By Pulin Bihari Sarkar and Tara Prasad Barat.

The luteo-cobaltic hydroxide, $[Co(NH_3)_6](OH)_3$, is a strong base like caustic soda and potash. The relative strengths of the cobaltammine bases have been determined by Lamb and Yngve (*J. Amer. Chem. Soc.*, 1921, **43**, 2352). The percentage ionisations at 0° and 0·00133*M* are as follows:—

$[Co(NH_3)_6]^{+++}$	$[Co(H_2O)(NH_3)_5]^{+++}$	$[Co(H_2O)_2(NH_3)_4]^{+++}$
89·5%	53·5%	24·6%
$[Co(En)_3]^{+++}$	$[Co(CO_3)(NH_3)_4]^{+}$	1:6 $[Co(NO_2)_2(NH_3)_4]^{+}$
88·6%	97·6 %	95·0%

The univalent bases, carbonato- and 1:6-dinitrito-hydroxides are as highly dissociated as alkali hydroxides, while the hexammine and triethylenediammine hydroxides have no parallel among the simple triacid inorganic bases (*e.g.*, aluminium—iron family and the rare earths) as regards solubility and extent of ionisation. The analogy with the alkalis persists even in the salts. Thus the chloroplatinates, chloroaurates, chloromercurates and fluosilicates are almost insoluble. Though the cobalt hexammines give insoluble neutral oxalates like the rare earths, their carbonates and bicarbonates, sulphites and phosphates, on the other hand, are very soluble like those of the alkalis. Further there exists a number of acid salts of the hexammine bases. Like the alkali sulphates, hexammine cobaltic sulphate gives insoluble double sulphates with the sulphates of the rare earths of the type—

$$[Co(NH_3)_6]_2(SO_4)_3,\ 3M_2(SO_4)_3,\ H_2O.$$

where M=La, Ce, Pr, Nd, Sm etc.

The present work was undertaken to precise the analogy of the hexammine bases with the alkalis by studying in detail the double salts of the cobalt hexammine series.

It has been observed that hexammine cobaltic sulphate forms double salt with ammonium sulphate and acid salts with sulphuric acid. The double salt of the hexammine cobaltic sulphate with ammonium sulphate of the formula $[Co(NH_3)_6]_2(SO_4)_3$, Am_2SO_4, $8H_2O$ was prepared by Klobb (*Bull. Soc. franc. Min.*, **24**, 307) who obtained it by crystallisation of a solution of hexam-

mine cobaltic sulphate containing an excess of ammonium sulphate. A preliminary experiment performed here showed however that the double salt is stable only within a narrow range of concentration. Ammonium sulphate, as is well known, is perfectly isomorphous with the sulphates of potassium, rubidium, caesium and mono-valent thallium. It is therefore expected that their sulphates will also yield corresponding double salts with hexammine cobaltic sulphate. Attempts to prepare these double salts in a pure state, by using equimolecular and excess concentrations, were unsuccessful.

It was therefore resolved to study the equilibrium of the ternary system consisting of hexammine cobaltic sulphate, potassium sulphate and water at 35° and to arrive, if possible, at the conclusion whether the double salt of hexammine cobaltic sulphate with potassium sulphate exists or not, and if so, what is its range of stability.

Experimental.

Method of Preparation.—Spontaneous oxidation of ammoniacal salt solution containing cobalt gives rise to luteo-cobaltic salts. The yield however is very poor, eighty per cent. of the total cobalt remaining in the solution as aquopentammine salts. The yield is higher if the oxidation be more vigorous.

Our starting material was pentahydrated hexammine cobaltic sulphate, which was prepared by the method of Klobb (*Bull Soc. chim.*, 1901, **25**, 102). The best yield could be obtained by maintaining a high concentration of ammonia and cooling the solution to 0° when passing the current of air. The crude salt which is sometimes mixed with its double salt with ammonium sulphate was purified by two or three crystallisations from hot water. The following is a typical analysis of the salt used. (Found: Co, 17·01 ; SO_4, 40·89. $[Co(NH_3)_6]_2(SO_4)_3,5H_2O$ requires Co, 16·86 ; SO_4, 41·15 per cent.) .

"Extra pure" potassium sulphate was recrystallised for use.

Method of Analysis.—The cobalt in solution was determined by electro-analysis. The total sulphate in solution after removal of cobalt was estimated as barium sulphate and from these figures the potassium was computed by difference.

The cobalt was deposited as metal on a weighed platinum gauze cathode, from a strongly ammoniacal solution containing

excess of ammonium salts. By electrolysing the solution, at 50°-60° with a current of 1-2 amperes, and using a rotating anode, the whole operation can be finished within an hour. For obtaining a bright and coherent deposit of the metal, excess of ammonia and ammonium salts are required, because cobalt has a tendency to deposit as black $Co(OH)_3$ on the anode.

Equilibrium determinations.

The procedure adopted was to weigh the constituents in definite proportions and to make the solution to 75 c.c. with water, at some temperature above 35° in a bottle of about 100 c.c. capacity provided with a tight-fitting glass stopper. The bottle was vigorously shaken in an electric shaker and then placed in a thermostat regulated at $35{\cdot}0 \pm 0{\cdot}1°$. The shaking was carried out mechanically for several days until equilibrium was attained, as indicated by no further change in the composition of the solution. During this time a soild phase or phases separated out. In the case of the solution containing posassium sulphate only the initial saturation was carried out at 80°. After the solid phase had been allowed to settle, about 10 c.c. of the clear solution were pipetted off, weighed and analysed. The solid phase was analysed after equilibrium had been attained. The solid phase was rapidly poured on a small Buchner funnel and drained by suction. About 0·5 g. of it was accurately weighed out, dissolved in water and analysed. Extreme care should be taken that the liquid adhering to the separated solid phase, shall be typical of the liquid phase with which it was in equilibrium. This mixture is usually known as the "rest." If there is any delay in filtration and weighing, appreciable evaporation will ensue and the "rest" will not consist of the mixture of phases which were in equilibrium. For the remainder of the system, mixtures of weighed quantities of potassium sulphate and hexammine cobaltic sulphate in amounts which were thought to be slightly greater than those necessary to saturate about 75 c.c. of water at 35° were carefully dissolved by raising the temperature to 50°. The solution was then shaken as before and placed in the thermostat. Equilibrium was much more quickly attained when potassium sulphate or hexammine cobaltic sulphate crystallised out than when the double salt. In the case of the double salt, shaking had to be carried on for more than a week. It was also found out that the supersaturated solution of the double salt attained equilibrium with remarkable slowness. In only a few

cases was it found that the pure double salt crystallised out in sufficient quantity. The results of the analysis of various saturated solutions and their corresponding "rests" are given in the following table

TABLE I.

I = Percentage composition of anhydrous K_2SO_4.
II = Percentage composition of anhydrous $[Co(NH_3)_6]_2(SO_4)_3$.
III = Grams of water per 100 g. of anhydrous salt, the solution being saturated with one of the two.

Liquid phase.			*Rests.*			*Solid phase.*
I	II	III	I	II	III	
100	0	721	—	—	—	K_2SO_4
92	8	634·6	99·68	0·32	9·2	
85	15	581	99	1	29	
78·6	21·4	527·8	98·9	1·1	23	
73·5	26·5	505	98·7	1·3	21·5	
71·21	28·79	485·6	81·35	18·65	15·95	K_2SO_4 + Double salt.
69·82	30·18	410	71·9	28·1	14·8	
67·9	32·1	402	64	36	12·1	
67·45	32·55	400·5	39·1	60·9	15·8	
67	33	400	23·18	76·82	16·7	Double salt.
66·04	33·96	392	23·06	76·94	21·5	
64·7	35·3	405	22·87	77·13	29·8	
62·5	37·5	420	22·28	77·72	21·6	
59·85	40·15	555	16·8	83·2	18·1	Double salt + $[Co(NH_3)_6]_2(SO_4)_3$
58	42	638	6·43	93·57	19·2	
54·01	45·99	928	3·5	96·5	19·8	
53	47	1104	2·3	97·7	17	
53·2	46·8	1206	1·8	98·2	18·9	
52·11	47·89	1380	1	99	28·8	$[Co(NH_3)_6]_2(SO_4)_3$
51·3	48·7	1428	0·8	99·2	19·3	
44	56	1846	0·7	99·3	27·1	
32·1	67·9	2607	0·71	99·29	23·95	
20·92	79·08	3324	0·69	99·31	18·2	
10·2	89·8	4065	0·38	99·62	18·75	
0	100	4754	0	100	17·6	

These results are best shown graphically using the method of representation of Janecke (*Z. anorg. Chem.*, 1906, **51**, 132), the units taken being grams instead of molecules. The abscissa indicates the number of grams of K_2SO_4 and $[Co(NH_3)_6]_2(SO_4)_3$ in 100 grams of dissolved anhydrous salt, and the ordinate shows the number of grams of water in which 100 grams of the mixture dissolve to give a saturated solution. It will be observed that the straight line joining the points, indicating the composition of the mother-liquor and the corresponding "rests" all pass through the point which indicates the composition of the solid phase and with which the various liquid phases are in equilibrium.

The line *AB* represents supersaturated solutions which are in equilibrium with one solid phase—pentahydrated hexammine cobaltic sulphate. The composition of the solid phase represented by the point (*a*) is on the ordinate, showing that the solid salt is hydrated. At *B* two solid phases—hexammine cobaltic sulphate and the double salt—separate out, the composition of the "rest" being shown by the point (*b*). The point *B* is therefore invariant. The line *BC* represents saturated solutions which are in equilibrium with the double sulphate, the point (*s*) representing the composition of the pure double salt. This point is within the curve and not on the abscissa, showing thereby that the double salt is hydrated. Unfortunately, the solubility difference of potassium sulphate and hexammine cobaltic sulphate is so very great that it is not possible to show from the graph the exact composition of the solid phases. The composition of the "rests" at (*c*) indicates that two solid phases—the double salt and potassium sulphate—have crystallised out. *CD* represents solutions which are saturated with respect to potassium sulphate. The point (*d*) representing the composition of all such solid phases is on the origin, showing that the solid phase is anhydrous.

According to this method of representation, 22·2 g. of K_2SO_4 and 77·8 g. of $[Co(NH_3)_6]_2(SO_4)_3$ represent molecular proportions. At points within the range *BC* the "rests" do not always consist of the pure double salt. For those systems the composition of whose liquid phase lies within the narrow range of 33—37·5 per cent $[Co(NH_3)_6]_2(SO_4)_3$, the solid phase in equilibrium, consists of the pure double salt. For making a detailed study of this short range, mixtures of $[Co(NH_3)_6]_2(SO_4)_3$, $5H_2O$ and K_2SO_4 were taken in definite proportions, the composition

of the successive mixtures varying by 1 per cent. It has been found that the pure double salt is only obtained when the proportion of $[Co(NH_3)_6]_2(SO_4)_3$, $5H_2O$ in the original mixture lies between 43 and 47 per cent.

The Double Salt, $[CO(NH_3)_6]_2(SO_4)_3$, K_2SO_4, $4H_2O$.

The pure double salt has been obtained by dissolving 5·5 g. of potassium sulphate and 4·4 g. of pentahydrated hexammine cobaltic sulphate in the smallest quantity of water at 60° and allowing it to crystallise. The double salt produces very characteristic well defined shining yellow crystals. The product is soluble in water but the original salt cannot be recovered by crystallisation, the salt being decomposed. On evaporation less soluble $[Co(NH_3)_6]_2(SO_4)_3$,$5H_2O$ crystallises out. The sample was air dried to constant weight and analysed. (Found: Co, 13·68; SO_4, 44·55; K_2SO_4, 20·1. $[Co(NH_3)_6]_2(SO_4)_3$.K_2SO_4,$4H_2O$ requires Co, 13·78; SO_4, 44·86; K_2SO_4, 20·33 per cent.).

For determining the water, a weighed quantity of the air-dried sample was placed in a thermostat and the temperature gradually increased to 110°. (Found: H_2O, 8·56. $[Co(NH_3)_6]_2(SO_4)_3$, K_2SO_4, $4H_2O$ requires H_2O,8·4 per cent.).

Summary.

The existence of the above salt and its range of stability in solution at 35° have established in the isotherm drawn according to the method of graphical representation of Janecke (*loc. cit.*). It has been found that from supersaturated solutions containing potassium sulphate hexammine cobaltic sulphate and water, the following phases will crystallise out at 35°.

(1) K_2SO_4, if the percentage of $[Co(NH_3)_6]_2(SO_4)_3$ in the solute does not exceed 28 per cent.

(2) Mixtures of K_2SO_4 and double salt, if the amount of $[Co(NH_3)_6]_2(SO_4)_3$ in the solute lies between 28 and 33 per cent.

(3) Pure double salt, if the amount of $[Co(NH_3)_6]_2(SO_4)_3$ in the solute lies between 33 and 37·5 per cent.

(4) Mixture of the double salt and $[Co(NH_3)_6]_2(SO_4)_3$ if the amount of latter in the solute lies between 37·5 and 46·8 per cent.

(5) Pure $[Co(NH_3)_6]_2(SO_4)_3$, $5H_2O$ if its amount in the solute exceeds 46·8 per cent.

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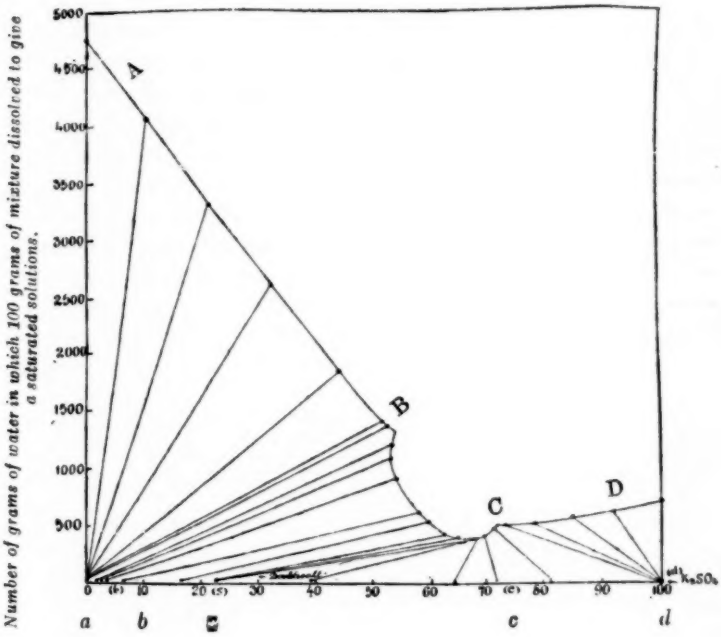
Number of grams of water in which 100 grams of mixture dissolved to give a saturated solutions.
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
A
B
C
D
0
10
20
30
40
50
60
70
80
90
100
a
b
c
d

FIG. 1.

A Method for the Determination of Copper in Commercial Aluminium.

By Jogesh Chandra Ghosh.

Copper in commercial aluminium is usually estimated by dissolving out the aluminium by means of caustic soda or sodium carbonate solution followed by any standard volumetric or colorimetric method (Lunge, "Technical Methods of Chemical Analysis," Vol. II, Part I, p. 347). It has now been found that aluminium may be completely brought into solution by means of dilute sulphuric acid leaving behind copper which may amount to the extent of 5 per cent. in the commercial samples. The accuracy of the results obtained by the present method compares very favourably with that of the existing methods. The following table gives the data obtained by the different methods.

Sample.	Cu by H_2SO_4 method.	Cu by NaOH method.	Cu by H_2S method.
Indian aluminium	0·20 %	0·22 %	0·20 %
English aluminium	1·02	1·03	1·00
Pig aluminium (toothed bar.)	0·30	0·30	0·20
,, ,, ,,	0·22	0·22	0·24
,, ,, ,,	4·58	4·62	4·61
,, ,, ,,	0·82	0·815	0·80
,, ,, ,,	1·15	1·13	1·12
,, ,, ,,	0·100	0·096	0·095*
,, ,, ,,	0·658	0·655	0·690
Shot aluminium	0·067*	0·065*	0·068*

* colorimetrically

Experimental.

The experimental procedure is as follows:—

About 2 g. of very thin drillings or shavings of the sample are introduced into a beaker (250 c.c.) and 100 c.c. of sulphuric acid (1 part concentrated acid of density 1·84 and 5 parts water) are added. The beaker, covered by means of a clock glass, is then allowed to simmer on a hot plate or burner taking care that the volume of the solution does not get below 75 c.c. Should this happen, water may be added. When all the aluminium has gone into solution, the beaker is removed from the source of heat and the contents quickly filtered and washed thoroughly with cold water till free from acid. A small hole is then made in the apex of the filter paper and the residue washed down into a beaker. About 5 c.c. of warm concentrated nitric acid are added through the sides of the filter paper which is again washed with hot water till free from acid, care being taken that the volume does not exceed 50 c.c. The copper is then brought into solution by heating and the nitrous fumes are removed by boiling. The copper is then estimated iodometrically by Low's method after neutralisation of the acid by ammonia.

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Velocity of Reaction in Mixed Solvents. Part II. The Velocity of Reaction between Sodium Thiosulphate and Alkyl Iodides in Organic Solvents—Water Mixtures.

By Mata Prasad and R. D. Godbole.

It has been shown in Part I (*J. Indian Chem. Soc.*, 1930, **7**, 59) that the velocity of reaction between potassium persulphate and potassium iodide in water is lowered by the addition of alcohol, glycerol, glycol and pyridine, and that no simple relation exists between velocity constants and the viscosities and the dielectric constants of the mixtures.

In the present investigation the reaction between alkyl iodides and sodium thiosulphate has been studied in mixtures of organic solvents and water. The kinetics of the reactions between sodium thiosulphate and alkyl iodides in aqueous solutions have been studied by Slator (*J. Chem. Soc.*, 1904, **85**, 1285). It was found that the order of the reaction is second as expected from the equation of the reaction,

$$Na_2S_2O_3 + RI = NaI + NaRS_2O_3.$$

Experimental.

The velocity of reaction between methyl and ethyl iodides with sodium thiosulphate has been studied in mixtures of water with methyl, ethyl, *n*- and *iso*-propyl alcohols, glycerol and glycol.

Methyl and ethyl iodides were prepared and purified in the laboratory and their purity was tested by determining their boiling points. Sodium thiosulphate used was Merck's "extra pure" chemical. All the organic solvents used were Merck's "extra pure" chemicals. Alcohols were further purified by distillation over calcium chloride.

Solutions of sodium thiosulphate and alkyl iodides were prepared in water, redistilled from alkaline potassium permanganate, fresh every time an experiment was performed. A known amount of the organic solvent was added to one of the solutions and the two solutions were kept separately in a thermostat maintained at 25° and were mixed together when they had acquired the temperature of the bath.

5 C.c. of the reaction mixture were taken out in ice-cold water at definite intervals of time and the amount of sodium thiosulphate

present in the solution was immediately determined by titration against standard iodine.

The velocity constant, K, of the reactions was then calculated from the bimolecular formula,

$$k = \frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

where a = initial concentration of sodium thiosulphate in terms of c.c. of iodine solution.

b = initial concentration of methyl iodide in terms of c.c. of iodine solution.

x = the amount of the iodine used up in terms of iodine solution in time t,

$$c = \frac{1}{t} \log \frac{b(a-x)}{a(b-x)} = k(a-b).$$

The results obtained with methyl and ethyl iodides are given below.

Mythyl Iodide and Sodium Thiosulphate.

In order to avoide the loss of methyl iodide due to evaporation in aqueous and aqueous alcohol solutions with low contents of alcohols, the reactions were carried out in a special type of vessel, shown in Fig. 1. With higher contents of alcohols ordinary conical flasks with rubber stoppers were used, for in these solutions there is no loss of methyl iodide due to evaporation.

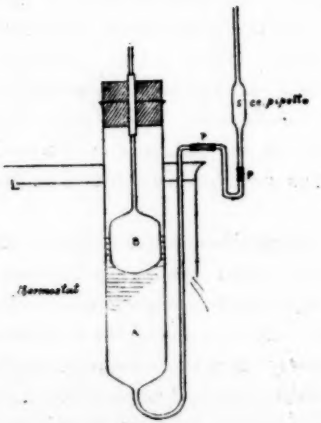

FIG. 1.

The wide glass tube *A* contained the solutions used in the experiments and was connected with a 5 c.c. pipette in such a manner that exactly 5 c.c. of the reaction mixture could be easily taken out. Evaporation from the surface was prevented by means of the float *B*.

The concentrations of sodium thiosulphate and methyl iodide used in the experiments were 0·03454*N* and 0·03408*N* respectively. The values of *a*, *b* and *x* are expressed in terms of c.c. of 0·009247 *N* solution of iodine required for 5 c.c. of the reaction mixtures.

TABLE I.

Solvent – Water.

t.	$a-x$.	x.	$b-x$.	$c \times 10^4$.
4	16·25	2·43	15·98	20·0
10	14·1	4·58	13·83	19·0
20	11·78	6·98	11·48	19·0
31	9·58	9·70	9·31	19·6
40	8·21	10·47	7·94	20·1

Mean value of $c \times 10^4 = 19·5$.

Mean value of $k \times 10^4 = 7·22$
Duplicate ,, $= 7·28$
Mean ,, ,, $= 7·25$

TABLE II.

Mean Values of $k \times 10^4$.

Organic solvent.	Percentage of the organic solvent.						
	0	10	20	30	40	50	60
Methyl alcohol ...	7·25	16·3	19·1	—	30·2	37·9	43·0
Ethyl alcohol ...	7·25	15·8	22·8	32·8	38·9	36·5	36·4
n-Propyl alcohol ...	7·25	18·7	23·5	18·9	14·7	—	11·7
*iso*Propyl alcohol ...	7·25	17·1	25·9	29·2	25·2	22·0	19·2
Glycol ...	7·25	6·18	—	—	—	—	—
Glycerol ...	7·25	5·66	—	—	—	—	—

The velocity constants have been plotted against the composition of the mixtures and the curves obtained are shown in Fig 2.

Velocity Constant—Composition Curves
(Methyl iodide–Sodium thiosulphate).

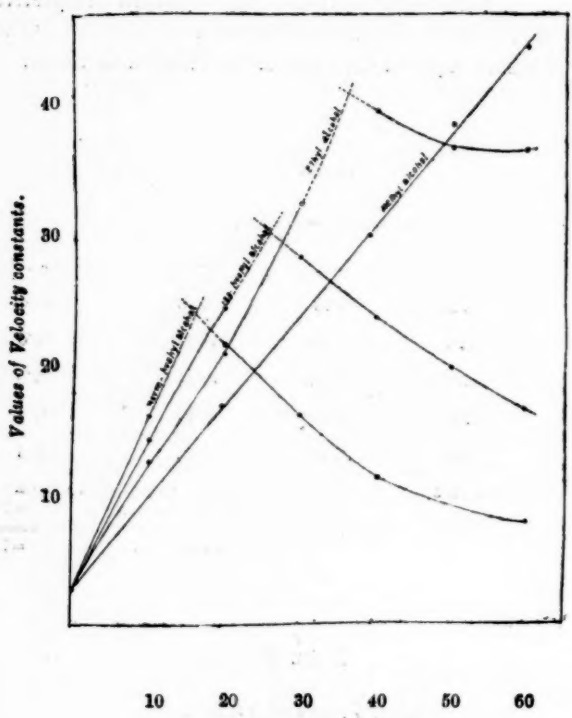

FIG. 2.

Ethyl Iodide and Sodium Thiosulphate.

Ethyl iodide is not so volatile as methyl iodide and hence reactions were carried out in conical flasks.

Concentrations of ethyl iodide and sodium thiosulphate used were 0·02582N and 0·03455N respectively. The values of a, b and x are expressed in terms of c.c. of 0·007463N solution of iodine required for 5 c.c. of the reaction mixture.

TABLE III.

Solvent—Water.

	$a-x$.	x.	$b-x$.	$c \times 10^5$.
20	20·18	0·60	14·75	22·5
40	19·75	1·03	14·32	20·0
60	19·32	1·46	13·89	20·0
80	18·84	1·94	13·41	20·0
100	18·41	2·37	12·98	20·0
125	17·91	2·87	12·48	20·2
145	17·49	3·29	12·06	20·5

Mean value of $c \times 10^5 = 20{\cdot}5$ Mean value of $k \times 10^4 = 3{\cdot}8$.

TABLE IV.

Mean Values of $k \times 10^4$.

Organic solvent.	Percentage of the organic solvent.						
	0	10	20	30	40	50	60
Methyl alcohol ...	3·8	—	6·77	—	8·74	—	10·8
Ethyl alcohol ...	3·8	7·42	10·0	12·30	12·30	10·40	—
n-Propyl alcohol ...	3·8	7·56	9·16	5·56	3·51	2·44	—
*iso*Propyl alcohol ...	3·8	8·47	11·5	9·66	6·22	4·64	—

The velocity constants have been plotted against the composition of the mixtures and the curves obtained are shown in Fig. 3.

Velocity Constant Composition Curves
(Ethyl iodide and Sodium thiosulphate).

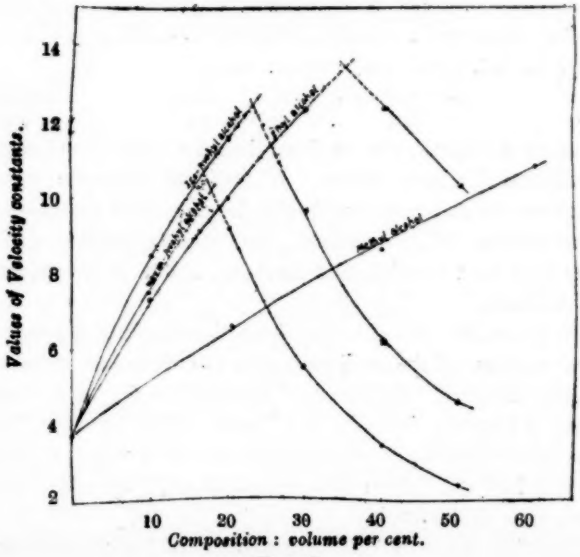

FIG. 3.

Discussion of Results.

Results described in the Tables II and IV show that the velocity constant varies as the composition of the medium in which the reaction is taking place is varied. Higher concentrations of the solvent than 60 per cent. could not be used due to the insolubility of sodium thiosulphate in mixtures containing more than 60 per cent. of the organic solvent.

But it will be seen from Figs. 2 and 3 that as the concentration of alcohols in the mixtures is increased, the value of the velocity constants at first increases and then begins to decrease (*cf.* maximum points A and B in the curves 2 and 3). Methyl alcohol is an exception to the above generalisation; no maximum point is observed in this case but the velocity constant continually increases with the increase in the concentration of methyl alcohol in the mixture. It is possible that the maximum point may also be obtained in this case at higher concentrations of the mixtures.

The maximum values of the velocity constants of the two reactions in various alcoholic mixtures decrease as

$$CH_3OH > C_2H_5OH > iso\text{-}C_3H_7OH > n\text{-}C_3H_7OH.$$

The increase in the number of OH-groups in the molecule of the solvent also decreases the accelerating effect. The mean values of the velocity constants in reaction mixtures containing 10 per cent. of methyl alcohol, glycol and glycerol are—

Solvent.	Methyl alcohol.	Glycol.	Glycerol.
$k \times 10^4$	16·3	8·1	5·66

Dielectric constant of the medium does not seem to influence the rate of reaction to a great extent. Whereas the dielectric constants of alcohol—water mixtures continually decrease with the increase in the concentration of the alcohol, the velocity constants in these reactions have been found first to increase, reach a maximum and then to decrease.

But it is possible that the rate of reaction may not depend on the dielectric constant of the medium but on the dielectric constant of the reaction mixture. Ionisation of electrolytes, *i.e.*, the electrical resistance of a system depends to a great extent on the dielectric constant of the system; hence the electrical resistances of mixtures of methyl iodide and sodium thiosulphate in aqueous ethyl alcohol mixtures were determined.

The reaction mixtures were prepared in the same manner as in the experiments described above. The resistance was measured by

Kohlrausch's bridge method at 25°. It was found that as the reaction proceeded, the resistance of the system gradually increased but the total increase was not more than 3–4 ohms. The resistances of the reaction mixtures in various ethyl alcohol—water mixtures at the start of the reaction are as follows:—

Percentage composition ...	10	20	30	40	50
Resistance in ohms ...	90·4	118·1	176·0	219·7	259·0

These values were plotted against composition and a straight line curve was obtained as shown in Fig. 4. This indicates that the

Resistance—Composition Curves of the System
$Na_2S_2O_3$ + MeI *in water–ethyl alcohol mixtures.*

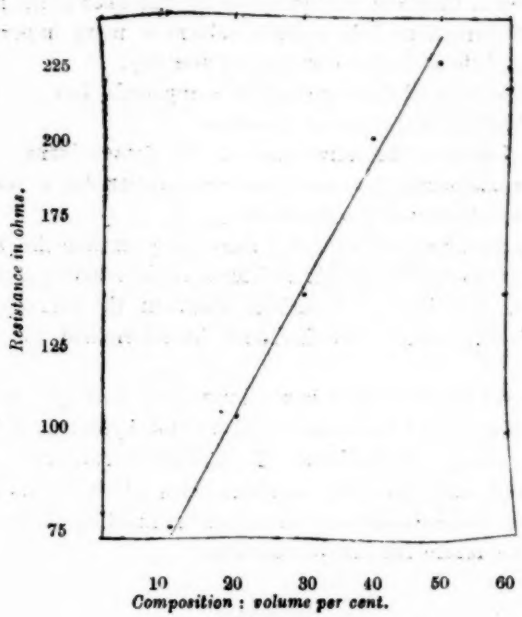

FIG. 4.

resistance of the reaction mixture increases regularly with the increase in the concentration of the alcohol in the mixtures. These results show that the causes responsible for the maximum points in the velocity constant—composition curves in no way influence the total resistance of the system.

It will be seen from the following table that the maximum points occur at the composition of the alcohol-water mixtures corresponding

to the composition of the known hydrates of alcohol in aqueous solution in the mobile state (*cf.* Salazar, *Anal. Fis Quim.*, 1921, **22**, 275).

TABLE V.

$CH_3I + Na_2S_2O_3$.			$C_2H_5I + Na_2S_2O_3$.		
Hydrate.	Theoretical composition.	Composition of maximum points.	Hydrates.	Theoretical composition.	Composition of maximum points.
EtOH, $6H_2O$	36·24 %	36 %	EtOH, $6H_2O$	36·24 %	35·2 %
PrOH, $16H_2O$	20·17 %	18 %	PrOH, $16H_2O$	20·17 %	18 %

It appears, therefore, probable that the influence of the molecular compound formation of the organic solvent is more important than the effect of the dielectric constant or viscosity.

The formation of these molecular compounds has got, probably, a two-fold effect on the rate of reaction.

1. It decreases the active mass of the free solvent. This will have an accelerating effect on the rate of reaction due to the increase in the concentration of the reactants.

2. Hydrated molecules, being more complex than the molecules of single solvents, offer greater resistence to the reacting molecules or ions. This will have a retarding effect on the rate of reaction.

The observed effect will, therefore, be determined by these two factors.

Jones and his co-workers have shown that ions get hydrated in aqueous solution and molecules are either not hydrated or hydrated to a small extent. Goldschmidt (*Z. physikal. Chem.*, 1907, **60**, 728) has assumed that ions also combine with alcohols and form ion-alcoholates. These effects will decrease the mobility of the ions and may further retard the rate of reaction.

Summary.

1. Reactions between sodium thiosulphate and methyl and ethyl iodides have been studied in various organic solvents and water mixtures.

2. Organic solvents have been found to exert a definite influence, acceleration or retardation.

3. There is no direct relationship between the velocity constants of the reactions in these mixtures and their composition.

4. In a homologous series of solvents the addition of the CH_2-group in the molecule of the solvent regularly accelerates or retards the rate of reaction.

5. Increase of OH-groups in the molecule of the solvents decreases the velocity constant.

6. Viscosity and dielectric constant of the mixture do not produce any appreciable effect.

7. Maximum points in the velocity constant and composition curves correspond to molecular compounds of the organic solvents with water.

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A Study of the Interaction between Thionyl Chloride and Substances Containing the Reactive Methylene Group. Part I. The Formation of Sulphoxides.

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During the investigations of the reaction between sulphuryl chloride and substances containing the reactive methylene ($-CH_2-$) group, it was observed that sulphuryl chloride invariably acts as a chlorinating agent (Naik and Shah, *J. Indian Chem. Soc.*, 1927, **4**, 11). It was, therefore, thought interesting to investigate the action of thionyl chloride on these substances, specially as it reacts with other compounds, giving rise to various products depending upon the conditions of the experiments.

The reactions of thionyl chloride may be roughly divided under three different heads. It reacts as—

(*i*) A chlorinating agent replacing groups such as (*a*) $-OH$, (*b*) $-SH$, (*c*) $-NO_2$, (*d*) $-SO_3H$, and (*e*) $-H$ by chlorine (Meyer, *Monatsh.*, 1901, **22**, 415; D. R. P. 201325-6, Frankland and Garner, *J. Chem. Soc.*, 1914, **105**, 1101; Barbier and Locquin, *Bull. Soc. chim.*, 1912, **11**, 223; Stähler and Schirm, *Ber.*, 1911, **44**, 319; McKenzie and Clough, *J. Chem. Soc.*, 1913, **103**, 687; Barger and Ewins, *ibid*, 1908, **93**, 735; Silberrad, *ibid*, 1921, **119**, 2029; Meyer, *Monatsh.*, 1915, **36**, 723; Pollak and Rudich, *ibid*, 1922, **43**, 2029; Majima and Simanuki, *Proc. Imp. Acad. Tokyo*, 1926, **2**, 544).

(*ii*) A dehydrating agent (Denham and Woodhouse, *J. Chem. Soc.*, 1913, **103**, 1861; Michaelis and Sieber, *Annalen*, 1893, **274**, 312; Meyer, *Monatsh.*, 1902, **23**, 897; Lasch, *Monatsh.*, 1913, **34**, 1653; Pawlewski, *Bull. Acad. Sci. Cracow*, 1903, 8; Wohl, *Ber.*, 1909, **40**, 4698).

(*iii*) A "thionating" agent giving rise to sulphonium chlorides, sulphoxides and sulphides (Colby and McLoughlin, *Ber.*, 1887, **20**, 195; Parker, *Ber.*, 1890, **23**, 1844; Smiles and Bain, *J. Chem. Soc.*, 1907, **91**, 1718; Gazdar and Smiles, *J. Chem. Soc.*, 1910, **97**, 2249; Smiles and Le Rossignol, *J. Chem. Soc.*, 1906, **89**, 697; 1908, **93**, 745; Michaelis and collaborators, *Ber.*, 1890, **23**, 3480; 1891, **24**,

745; 1893, **26**, 2158; 1897, **30**, 1009; *Annalen*, 1893, **274**, 173, 187, 200; Francke, *Ber.*, 1898, **31**, 2178; Rosenheim and Sarow, *Ber.*, 1905, **38**, 1298; Green, *J. Chem. Soc.*, 1924, **125**, 1450).

It is thus evident from the literature that thionyl chloride will react in a very interesting manner, as it does with phenols and amines with which the reactive methylene ($-CH_2-$) group has many points of similarity in reaction. With these ideas in view, the reaction of thionyl chloride was studied first on malon-diphenylamide in presence of dry benzene. A vigorous evolution of hydrochloric acid gas took place, changing the colour of the solution to red, which gave yellowish-red needles. The course of the reaction may be given as follows:—

$$(RNH{\cdot}CO)_2CH_2 + SOCl_2 = (RNH{\cdot}CO)_2C{:}SO + 2HCl$$

(where R = phenyl, tolyl, xylyl or α-naphthyl groups or one of the R is a hydrogen.)

The above constitution of the compound follows from the following considerations:—

(*i*) That the two hydrogen atoms are not supplied by the phenyl group, because—

(*a*) Malon-dimethylamide, which possesses no such phenyl group, gives the compound $SO:[CH(CO{\cdot}NHCH_3)_2]_2$.

(*b*) Malon-monophenylamide which possesses only one phenyl group, gives the compound, malon-monophenylamide sulphoxide. If the phenyl group be reactive such a compound cannot be expected.

(*c*) The sulphoxides obtained are very unstable whereas those having the grouping $-SO-$ in the nucleus are very stable (Colby and McLoughlin, Parker, *locc. cit.*).

(*ii*) That the hydrogen atoms eliminated are not those that are attached to the nitrogen atom of the $-NHR$ group, because—

(*a*) Malon-dimethylphenylamide, which contains no such amido-hydrogen, reacts with thionyl chloride.

(*b*) Only one hydrogen is replaced in malon-dimethylamide, though it contains two such amido-hydrogens.

Thionyl chloride was made to react with the following amides:—

(1) Malon-diphenylamide, (2) malon-di-*o*-tolylamide, (3) malon-di-*m*-tolylamide, (4) malon-di-*p*-tolylamide, (5) malon-di-(1:4:5)xylidide, (6) malon-di-α-naphthylamide, (7) malon-di-β-naphthylamide,

(8) malon-mono-phenylamide, (9) malon-mono-*o*-tolylamide, (10) malon-mono-*m*-tolylamide, (11) malon-mono-*p*-tolylamide, (12) malon-mono-α-naphthylamide, (13) malon-mono-β-naphthylamide, (14) malon-di-methylphenylamide, (15) malon-*p*-tolylamate, (16) malon-*o*-tolylamate, (17) malon-dimethylamide, (18) malon-diethylamide, (19) malon-dipropylamide, (20 and 21) malon-dibutylamide (*n*- and *iso*-), (22) malonamide, and the amides of methylmalonic acid.

Of the above, (1) to (16) reacted to give sulphoxides

$$(RNH{\cdot}CO)_2CH_2 + SOCl_2 = (RNH{\cdot}CO)_2C{:}SO + 2HCl;$$

but in the case of amides (14), (15) and (16) the reaction products were liquids, which did not solidify even when kept in a freezing mixture. Hence they were not worked up for the present.

In the case of (17) and (18) only one hydrogen atom of the methylene group was found to be reactive, the reaction taking the following course:

$$2(CH_3NH{\cdot}CO)_2CH_2 + SOCl_2 = [(CH_3NH{\cdot}CO)_2CH]_2{:}SO + 2HCl.$$

This type of reaction is not unusual. Many instances may be cited in which only one hydrogen atom of the methylene group had become reactive. Sulphur monochloride reacted with malon-dimethylphenylamide giving a disulphide $[(Ph(Me)N{\cdot}CO)_2CH]_2S_2$ (Naik, *J. Chem. Soc.*, 1921, **119**, 379); a monochloro-derivative of the same was obtained by West (*J. Chem. Soc.*, 1922, **121**, 2196) by the action of free chlorine and by Naik and Shah (*loc. cit.*) by sulphuryl chloride on the same substance. Malon-dipropylamide monosulphonic acid was obtained by the action of chlorosulphonic acid on malon-dipropylamide (Naik and Shah, under publication). Such a type of reaction has generally been explained by supposing that the second hydrogen atom became sluggish after the first was replaced by the substituent. In the case of (22) no reaction takes place under the conditions generally observed in these experiments. In the case of all the remaining amides a vigorous evolution of hydrogen chloride was observed but no definite reaction product could be separated because in all probability the sulphoxides formed were decomposed during the precipitation, owing to the unstable nature of such compounds.

From the above results it can be seen that in a series like:—

(*i*) $CH_2(CO{\cdot}NH_2)_2$, (*ii*) $CH_2(CO{\cdot}NHCH_3)_2$, (*iii*) $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHR$, (*iv*) $CH_2(CO{\cdot}NHR)_2$, (*v*) $CO_2C_2H_5{\cdot}CH_2{\cdot}CO{\cdot}NHR$ the reactivity of the hydrogen atoms of the methylene group, which

is absent in (*i*), starts in (*ii*) and goes on increasing. This can be explained as the effect of the increase of the negative character of the two carbonyl groups adjacent to the reactive methylene group in all the compounds; for malonamide, in which the two amino-groups completely neutralise the negative character of the carbonyl groups attached to the methylene group, does not react with thionyl chloride, whereas, in all the other cases, the basic character of the substituted amino-groupings attached to the carbonyl group being progressively reduced, the hydrogen atoms of the reactive methylene group are thrown into reactivity with increasing vigour. This reactivity is seen enhanced, when one or both of the amino-groups are replaced by negative groups, like phenyl, tolyl, naphthyl, etc. In the case of (*v*) where one of the amino-groups is completely replaced by a carbethoxy group, the reaction is exceptionally vigorous.

Three different hypotheses are put forth to explain the course of the reactivity depending upon the total negativity, namely, (1) polarity hypothesis (Macbeth and collaborators, *J. Chem. Soc.*, 1922, **121**, 892, 904, 1109, 2169, 2527, 2601; 1923, **123**, 1121, 1925; 1925, **127**, 892, 1118; (2) keto-enol transformation (Thorpe and collaborators, *J. Chem. Soc.*, 1911, **99**, 2183; 1921, **119**, 1203; 1922, **121**, 1896); (3) the combined effect of polarity and steric hindrances as would give rise to keto-enol transformations (West, *J. Chem. Soc.*, 1924, **125**, 710). The course of the reaction in the case of the compounds investigated, can be represented on the keto-enol hypothesis. Taking the case of malon-diphenylamide (according to Norris and Thorpe),

$$PhNH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHPh \longrightarrow PhNH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}NHPh$$

$$SOCl_2\ PhNH{\cdot}CO{\cdot}CH{:}CO{\cdot}NHPh \longrightarrow PhNH{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}NHPh$$
$$\longrightarrow \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$$
$$\qquad\qquad\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad SOCl \qquad\qquad\qquad\qquad\qquad SOCl$$
$$\qquad\qquad\qquad\qquad (unstable)$$

The second hydrogen atom will again tautomerise and will remove the second chlorine atom, giving rise to $(C_6H_5NH{\cdot}CO)_2C{:}SO$. In the case of substances, where the second hydrogen atom remains sluggish, the second chlorine atom is removed by the other molecule.

It is interesting to observe that these sulphoxides give rise to sulphides, when heated with dry benzene in presence of a dry

catalyst such as hydrochloric acid gas and iodine. This will form a subject of a future communication.

Experimental.

Malon-diphenylamide sulphoxide.—Two g. of malon-diphenylamide were made to interact with 1·6 g. of thionyl chloride in presence of 25 c.c. of dry benzene, on a water-bath. After an hour and a half, when the evolution of hydrochloric acid had nearly ceased, the mixture was concentrated and the compound was precipitated by slow addition of dry petroleum (b.p. 50-60°). It came out in the form of yellowish-red needles. It was washed free from thionyl chloride by dry petroleum. It melted with decomposition at 129°. It is easily decomposed by water and alcohol giving the original amide and sulphur dioxide. (Found: S, 10·56; N, 9·52. $C_{15}H_{12}N_2O_3S$ requires S, 10·66; N, 9·32 per cent.).

Malon-di-o-tolylamide sulphoxide.—Three g. of the amide were allowed to react with 1·6 g. of thionyl chloride as above. It gave a deep red crystalline compound, melting at 129-30°. It is easily decomposed by water and alcohol. (Found: S, 9·61. $C_{17}H_{16}O_3N_2S$ requires S, 9·75 per cent.).

Malon-di-m-tolylamide sulphoxide.—It was prepared from 3 g. of the amide and 1·6 g. of thionyl chloride. It was a saffron coloured crystalline compound, which melted at 142-43°. It is decomposed by water and alcohol. (Found: S, 9·87. $C_{17}H_{16}O_3N_2S$ requires S, 9·75 per cent.).

Malon-di-p-tolylamide sulphoxide.—It was prepared like the above compound. It is a deep red crystalline compound. It decomposes above 170° and melts at 215°. It is decomposed by water and alcohol. (Found: S, 9·65. $C_{17}H_{16}O_3N_2S$ requires S, 9·75 per cent.).

Malon-di-α-naphthylamide sulphoxide.—It was similarly prepared from 3·4 g. of the amide and 1·6 g. of thionyl chloride. It came out in the form of charcoal-black needles. It decomposes at 165° and melts at 210°. It is decomposed by water and alcohol. (Found: S, 8·22. $C_{23}H_{16}O_3N_2S$ requires S, 8·00 per cent.).

Malon-di-β-naphthylamide sulphoxide.—It was prepared like the previous compound. They are deep red needle-shaped crystals. These decompose above 170° and melt at 199°. It is decomposed

by water and alcohol. (Found: S, 8·23. $C_{23}H_{16}O_3N_2S$ requires S, 8·00 per cent.).

Malon-di(1:4:5)-*xylidide sulphoxide*.—It was prepared from 3·1 g. of the amide and 1·6 g. of thionyl chloride. It gave deep red needles. They melt at 172-3°. It is decomposed by water and alcohol. (Found: S, 9·06. $C_{19}H_{20}O_3N_2S$ requires S, 8·96 per cent.).

Malon-monophenylamide sulphoxide.—It was prepared from 2 g. of the amide and 1·4 g. of thionyl chloride. Yellowish-red needles were obtained. The product melts at 150°. It is decomposed by water and alcohol. (Found: S, 14·54. $C_9H_8O_3N_2S$ requires S, 14·28 per cent.).

Malon-mono-p-*tolylamide sulphoxide*.—It was prepared from 2·1 g. of the amide and 1·4 g. of thionyl chloride. It came down in the form of chocolate coloured needles, m.p. 156-7°. It is decomposed by water and alcohol. (Found: S, 13·46. $C_{10}H_{10}O_3N_2S$ requires S, 13·44 per cent.).

Preparation of Malon-mono-m-*tolylamide*.—Ethyl malonate (25 g.) and *m*-toluidine (11 g.) were mixed in a round-bottomed flask, having a wide upright tube passing through the cork, fitted in the mouth of the flask. The length of the tube from the cork upwards to the bent, measured 15 cms. The flask was heated in a paraffin-bath maintained at a temperature of 120-125°. The rate at which the alcohol was allowed to distill was regulated in such a way that the ester got no chance of being distilled out. After heating for eight hours, the contents were transferred to a stoppered bottle and were mixed with twice its amount of ammonia (*d* 0·88). This was shaken for four hours. The semi-solid mass was transferred to a beaker and evaporated till it was nearly solid. This mass which was a mixture of malon-di-*m*-tolylamide, malon-mono-*m*-tolylamide and malonamide, was filtered at the pump after cooling and washed with ether to remove the unreacted amine. It was boiled with alcohol and water (1:6) and filtered hot. This kept the insoluble diamide on the filter paper. The liquid deposited white thick needles on cooling, the malonamide being kept in solution. The product melts at 165°. It is very soluble in hot water, methyl and ethyl alcohol, acetic acid, and sparingly so in cold water, hot benzene and hot carbon tetrachloride. It is insoluble in petroleum. (Found: N, 14·46. $C_{10}H_{12}O_2N_2$ requires N, 14·58 per cent.).

Malon-mono-m-*tolylamide sulphoxide*.—It was prepared like the previous sulphoxide. It gave yellowish-red needles, m.p. 140°. It is decomposed by water and alcohol. (Found: S, 13·45. $C_{10}H_{10}O_3N_2S$ requires S, 13·44 per cent.).

Malon-mono-o-*tolylamide*.—Ethyl malonate (25 g.) and *o*-toluidine (11 g.) were heated under the same conditions as stated above, and treated likewise. It gave thick white needles, m.p. 162°. It is soluble in hot water, methyl and ethyl alcohol, and acetic acid. It is sparingly soluble in cold water, hot benzene and carbon tetrachloride, and insoluble in petroleum. (Found: S, 15·01. $C_{10}H_{12}N_2O_2$ requires N, 14·58 per cent.).

Malon-mono-o-*tolylamide sulphoxide*.—It was prepared from 2·1 g. of the amide and 1·4 g. of thionyl chloride. It formed deep red crystals, m.p. 168°. The product is decomposed by water and alcohol. (Found: S, 13·58. $C_{10}H_{10}O_3N_2S$ requires S, 13·44 per cent.).

Malon-mono-α-*naphthylamide*.—Ethyl malonate (25 g.) and α-naphthylamine (14·1 g.) were condensed under identical conditions. After the usual treatment, it gave reddish needles, which after recrystallisation melted at 146°. It is very soluble in hot water, methyl and ethyl alcohol and acetic acid, and sparingly so in cold water, hot benzene and carbon tetrachloride. It is insoluble in petroleum. (Found: N, 11·96. $C_{13}H_{12}O_2N_2$ requires N, 12·28 per cent.).

Malon-mono-α-*naphthylamide sulphoxide*.—It was prepared from 2·5 g. of the amide and 1·4 g. of thionyl chloride. It forms deeply coloured needles, melting at 170°. It is decomposed by water and alcohol. (Found: S, 11·92. $C_{13}H_{10}O_3N_2S$ requires S, 11·64 per cent.).

Malon-mono-β-*naphthylamide*.—Ethyl malonate (25 g.) and β-naphthylamine (14·1 g.) were similarly condensed and treated. The aqueous-alcoholic solution gave white leaflets, m.p. 188°. In solubility it resembles the previous amide. (Found: N, 12·32. $C_{13}H_{12}O_2N_2$ requires N, 12·28 per cent.).

Malon-mono-β-*naphthylamide sulphoxide*.—It was prepared like the last sulphoxide. It forms chocolate coloured needles, m.p. 160°. It is decomposed by water and alcohol. (Found: S, 11·87. $C_{13}H_{10}O_3N_2S$ requires S, 11·64 per cent.).

Bis-malon-dimethylamide sulphoxide.—Two g. of malon-dimethylamide sulphoxide were made to react with 1·8 g. of thionyl

chloride in 25 c.c. of dry benzene. After half an hour a white crystalline substance separated. When the evolution of hydrogen chloride had ceased, the reaction product was separated and filtered and washed with dry petroleum. It melts at 208°. It is sparingly soluble in benzene, but insoluble in toluene and petroleum. It is not decomposed by cold alcohol but is slowly docomposed by hot alcohol. (Found: S, 10·01. $C_{10}H_{18}O_5N_4S$ requires S, 10·45 per cent.).

Bis-malon-dimethylamide sulphoxide.—It was similarly obtained. It melts at 176°. The product is sparingly soluble in benzene and insoluble in toluene and petroleum. It is not decomposed by cold alcohol and water. (Found: S, 8·64. $C_{14}H_{26}O_5N_4S$ requires S, 8·84 per cent.).

The authors take this opportunity to express their gratitude to the Government of His Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work. One of the authors (M.M.P.) wishes to record his gratitude to His Highness the Maharaja of Bhavnagar for granting a scholarship, which enabled him to carry out the research.

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A Study of the Interaction between Thionyl Chloride and Substances Containing the Reactive Methylene Group. Part II. Conversion of Sulphoxides into Sulphides.

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While studying the action of thionyl chloride on malon-diphenylamide, it was found that if the reaction mixture was heated for more than four hours, a yellowish-white crystalline substance was precipitated. This compound was found to have the constitution, $(C_6H_5NH{\cdot}CO)_2C:S:C(CO{\cdot}NHC_6H_5)_2$ (I)

This behaviour of malon-diphenylamide is not surprising in view of the fact that thionyl chloride does react with different substances, giving rise to different products, depending on the conditions of the experiment (Michaelis and Philips, *Ber.*, 1890, **23**, 559; Sprauge, *J. Chem. Soc.*, 1891, **59**, 321; Jassinarri, *Gazzetta*, 1890, **20**, 362; Voswinkel, *Pharm. Z.*, 1895, **40**, 241; Loth and Michaelis, *Ber.*, 1894, **27**, 2540; Michaelis and Godchaux, *Ber.*, 1890, **23**, 553; Michaelis and Schindlar, *Annalen*, 1899, **310**, 137).

A sulphide similar to the above was also obtained by Michaelis and Philips (*loc. cit.*) by the interaction of thionyl chloride and acetoacetic ester, to which they attributed the constitution (II).

The course of the reaction was explained by them on the assumption that thionyl chloride decomposes into sulphur dichloride and sulphuryl chloride; and the sulphur dichloride thus formed reacts with the ester as under:—

$$2SOCl_2 = SCl_2 + SO_2Cl_2 \quad \ldots\ldots(1)$$

$$2\ \begin{matrix}CH_3CO\\CO_2Et\end{matrix}\!\!>\!CH_2 + SCl_2 = \left[\begin{matrix}CH_3CO\\CO_2Et\end{matrix}\!\!>\!CH\right]_2\!S + 2HCl \quad \ldots(2)$$

(II)

Michaelis and Loth observed that thionyl chloride reacted as under, with phenols, the final products of the reaction being sulphides:

$$2C_6H_5{\cdot}OH + SOCl_2 = (OH{\cdot}C_6H_4)_2SO + 2HCl \quad \ldots\ldots(3)$$

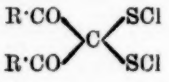
(A)

$$(OH{\cdot}C_6H_4)_2SO + SOCl_2 = (OH{\cdot}C_6H_4)_2S + SO_2 + Cl_2 \ldots\ldots (4)$$

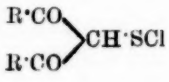
(B)

Here the formation of sulphides from sulphoxides was attributed by them to "the reducing action of thionyl chloride." This was supported by the fact that the substance (B), on treatment with nitric acid, gave the substance (A).

It must, however, be pointed out that the formation of the sulphides from sulphoxides, as observed here, cannot be explained on any of the above hypotheses. The hypothesis of Michaelis and Philips presupposes the assumption that thionyl chloride decomposes into sulphur dichloride and sulphuryl chloride. The reaction of sulphur dichloride with substances containing the reactive methylene group has already been studied in this laboratory by Naik and Jadhav (*J. Indian Chem. Soc.*, 1926, **3**, 261), and in no case was a sulphide of the type represented by Michaelis and Philips obtained, the compounds formed having the constitution—

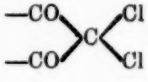


or



(C) (D)

Again Naik and Shah (*J. Indian Chem. Soc.*, 1927, **4**, 11) have observed during the investigation of the action of sulphuryl chloride on the same substances, that chloro-compounds of the type,



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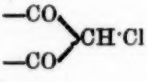

(E) (F)

are formed. Finally the chlorine disengaged as per (4) above would produce chloro-compounds similar to the above (*cf.* West, *J. Chem. Soc.*, 1924, **125**, 100). Had the course of the reaction been as represented by Michaelis and Philips or Michaelis and Loth, compounds of the type (C), (D), (E), or (F) should have been obtained, whereas during the present work no such compounds were isolated.

Further, if the reaction proceeded as represented by Michaelis and Loth, the resulting sulphide would possess the constitution (G), thus:

(G)

whereas the sulphides obtained here have the constitution,

$$(RNH{\cdot}CO)_2C:S:C(CO{\cdot}NHR)_2$$

That the sulphides have the constitution assigned to them as above follows from the fact that, thio-bis-malon-diphenylamide when hydrolysed with caustic alkali yields aniline as one of the products of hydrolysis. From this it is clear that the sulphur is neither attached to the nitrogen nor to any of the carbon atoms in the nucleus.

From the above considerations, one is led to suggest that the course of the reaction in the present case is entirely different from that represented by Michaelis and Philips or Michaelis and Loth. The formation of the sulphides from the sulphoxides can be well explained in the following manner:—

$$(RNH{\cdot}CO)_2C:S:O+O:S:C(CO{\cdot}NHR)_2=[(RNH{\cdot}CO)_2C]_2:S+SO_2$$

(H)

where R may be a tolyl, a phenyl or a naphthyl grouping.

This reaction may proceed either (*i*) spontaneously, or (*ii*) in the presence of a catalyst (here thionyl chloride acts as the catalyst). In order to decide this point freshly prepared malon-diphenylamide sulphoxide was heated in dry benzene solution (*a*) alone, (*b*) in the presence of thionyl chloride, (*c*) in the presence of dry hydrochloric acid gas, and (*d*) in the presence of iodine. In experiment (*a*) the original malon-diphenylamide was obtained back; whereas in all the other cases a distinct steady evolution of sulphur dioxide was perceived and the sulphide was isolated as the final product. This definitely points to the conclusion that the sulphides are formed from the sulphoxides under the influence of the catalysts such as, thionyl chloride, hydrochloric acid gas or iodine.

The investigation in connection with the formation of sulphides

from sulphoxides was carried out in the case of the sulphoxides obtained from the following amides:—

(1) Malon-diphenylamide, (2) malon-di-*o*-tolylamide, (3) malon-di-*m*-tolylamide, (4) malon-di-*p*-tolylamide, (5) malon di-α-naphthylamide, (6) malon-di-β-naphthylamide, (7) malon-monophenylamide, and (8) malon-mono-*m*-tolylamide.

In all the cases sulphides similar to (H) were obtained, except in (5) and (6), where besides these sulphides, by-products not containing sulphur and having melting points higher than those of the original amides were obtained. These are still under investigation.

Experimental.

Thio-bis-malon-diphenylamide (I).—Malon-diphenylamide (1·2 g.) was heated with thionyl chloride (0·9 g.) for four hours, after which a solid began to separate. The reaction was continued till there was no further separation of the solid. The compound was filtered after cooling, and washed with dry petroleum (b. p. 50°-60°). It was then boiled with dry petroleum to remove the adhering colour and crystallised from alcohol; m.p. 196°. It is fairly soluble in benzene, alcohol and acetic acid, but insoluble in petroleum and water. (Found: S, 6·07; N, 10·62. $C_{30}H_{24}N_4O_4S$ requires S, 5·96; N, 10·44 per cent.).

Action of dry Hydrochloric Acid on Malon-diphenylamide Sulphoxide.—One g. of freshly prepared sulphoxide was disolved in 25 c.c. of dry benzene and heated under reflux. Dry hydrochloric acid gas was then slowly passed through this solution. After some time a solid began to separate. The reaction was carried on till there was no evolution of sulphur dioxide. It was filtered and washed with petroleum; it was found to be identical with (I) obtained above.

Action of Iodine.—The above sulphoxide (1 g.) was dissolved in 25 c.c. of dry benzene and 0·4 g. of iodine was added to it. The mixture was heated under reflux for about half an hour, when a solid began to separate. When the evolution of sulphur dioxide had ceased, the compound was filtered and washed with alcohol. It was crystallised from alcohol and subsequently found to be identical with the thio-bis-malon-diphenylamide, obtained in the last two cases.

Hydrolysis of Thio-bis-malon-diphenylamide.—The thio-compound (8 g.) was refluxed with caustic potash (7 g.) dissolved in 10 c.c.

of water, for two hours. A heavy liquid separated out; the mixture was extracted with ether, which on evaporation left a liquid, which was identified as aniline. The aqueous solution was evaporated on a water-bath when a solid was obtained, which on treatment with hydrochloric acid evolved hydrogen sulphide. In all probablity the "thio"-grouping was decomposed during the hydrolysis giving rise to potassium sulphide, which evolved hydrogen sulphide.

Thio-bis-malon-di-o-tolylamide.—It was similarly prepared from 1·5 g. of the amide and 0·9 g. of thionyl chloride by heating for four hours The compound was crystallised from alcohol in white needles, m. p. 214°. It is soluble in alcohol and acetic acid but insoluble in petroleum and water. (Found: S, 5·07. $C_{34}H_{32}O_4N_4S$ requires S, 5·41 per cent.).

Thio-bis-malon-di-m-tolylamide.—It was prepared like the previous compound. The substance was precipitated by slowly adding the solution to a large amount of petroleum. This was repeatedly done by dissolving the compound in benzene and reprecipitating with petroleum till the melting point was constant. It is a dirty yellow substance. m. p. 164°. It is soluble in benzene and acetic acid but insoluble in petroleum. (Found: S, 5·45. $C_{34}H_{32}O_4N_4S$ requires S, 5·41 per cent.).

Thio-bis-malon di-p-tolylamide.—It was prepared as usual. The precipitated substance was filtered and washed with petroleum, and then boiled with alcohol to remove the adhering colour. It is a deep yellow substance and melts at 198°. It is very soluble in acetic acid and sparingly soluble in benzene and alcohol, but insoloble in petroleum. (Found: S, 5·71. $C_{34}H_{32}O_4N_4S$ requires S, 5·41 per cent.).

Thio-bis-malon- di-α-naphthylamide.—Malon-di-α-naphthylamide (1·7 g.) was refluxed in benzene with 0·9 g. of thionyl chloride, for four hours. A substance was precipitated, which was filtered. On examination it was found to contain no sulphur (m.p. 248°). The filtrate was then added to a large amount of petroleum, when a compound was precipitated. After repeated reprecipitations, it was found to melt at 132°. It is very soluble in benzene and acetic acid but insoluble in petroleum. (Found: S, 4·04. $C_{46}H_{32}O_4N_4S$ requires S, 4·34 per cent.).

Thio-bis-malon-di-β-naphthylamide.—This was prepared like the previous compound. The substance precipitated during heating contained no sulphur and melted at 265°. The "thio" compound was precipitated from the solution by petroleum. After purification it

melts at 146°. It is a dirty yellow substance soluble in benzene and acetic acid but insoluble in petroleum. (Found: S, 4·66. $C_{46}H_{32}O_4N_4S$ requires S, 4·34 per cent.).

Thio-bis-malon-monophenylamide.—It was prepared like the other thio-compounds. After repeated reprecipitations, it was found to melt at 114°. It is soluble in benzene and acetic acid but insoluble in petroleum. (Found: S, 8·46. $C_{18}H_{16}O_4N_4S$ requires S, 8·33 per cent.).

*Thio-bis-malon-mono-*m*-tolylamide.*—This was prepared as usual. It is a yellow substance, m.p. 123°. It is soluble in benzene and acetic acid but insoluble in petroleum and water. (Found: S, 7·58. $C_{20}H_{20}O_4N_4S$ requires S, 7·77 per cent.).

The authors desire to record their gratitude to the Government of His Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work. One of the authors (M.M.P.) also desires to express his gratitude to H.H. the Maharaja of Bhavnagar for a scholarship which enabled him to carry on this work.

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Studies in Azotriphenylcarbinol Dyes.

By Rajendra Nath Sen and (the late) Akshoy Kumar Sen.*

Considerable interest is attached to the investigation of the joint effect of different chromophores specially the azo- and triphenyl carbinol groups contained in the molecule of a dyestuff. This type of triphenylcarbinol dyes, containing one triphenylcarbinol group in the *para*-position to an azo-group and without any auxochromic group in the molecule, has been previously studied by Green and Sen (*J. Chem. Soc.*, 1912, **101**, 1113).

The effect of multiplying the number of chromophores, specially the azo-group, in this type of dyestuff has been ascertained later by Sen and Sett (*J. Amer. Chem. Soc.*, 1924, **46**, 111). Now further studies in azotriphenylcarbinol dyes have been made with a view (1) to ascertain the effect of the introduction of an additional triphenylcarbinol group on the colour and dying properties, and (2) to determine the influence of an additional auxochrome (OH) in the *para*-position to the azo-group.

The azotriphenylmethane dyestuffs, containing two triphenylcarbinol groups in the *para*-positions to the azo-group have been prepared by the condensation of the dialdehyde (azobenzaldehyde sulphonic acid, *J. Indian Chem. Soc.*, 1930, **7**, 14) with the hydroxy-acids such as, salicylic acid, 2-hydroxy-*m*-toluic acid and 2-hydroxy-*p*-toluic acid by means of concentrated sulphuric acid (*d* 1·84, free from nitric acid) in the cold. The reaction takes place between one molecule of the dialdehyde and four molecules of the hydroxy-acid. The leuco-compounds are oxidized to azotriphenylcarbinol compounds by means of sulphuric acid solution of nitrosyl sulphate. To complete the reaction it is necessary to warm the mixture to 50° for about 3 hours.

The leuco-compounds are yellow dyestuffs and produce on wool yellow shades considerably lighter than the shade (orange) obtained with the dialdehyde itself. This shows that too much complexity of the molecules seems to have an effect similar to that of too much multiplication of chromophores. It is a curious fact that only the leuco-compound of 2-hydroxy-*m*-toluic acid produces on

* The delay in the publication of the paper is due to the sudden death of one of the authors.

wool a pink shade even when it is prepared with exclusion of air in an atmosphere of carbon dioxide.

Wool is dyed directly in red shades by the carbinol dyes excepting that obtained from the leuco-condensation product of the dialdehyde with 2-hydroxy-*p*-toluic acid, which has very feeble dyeing properties and produces a light chocolate shade, showing the marked effect of the position of the CH_3-group on the colour and dyeing property. With different mordants on wool, different shades are produced: tin, bright red; copper, bluish-red; aluminium, reddish-violet; iron, reddish-black. It is very interesting to note that the yellow shade on wool, produced by the leuco-compounds, is changed to black on after-chroming, passing through violet to green (Green and Sen, *loc. cit.*).

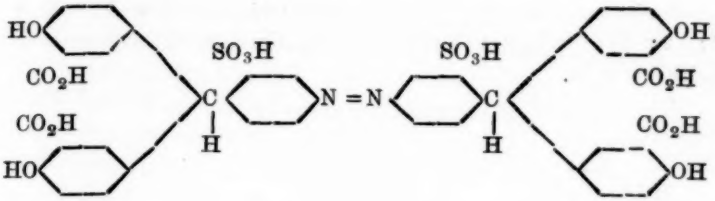
Next to study the influence of an additional auxochrome (OH) in the *para*-position to the azo-group, salicyl-azobenzaldehyde-sulphonic acid (*J. Indian Chem. Soc.*, 1930, **7**, 16) has been condensed with the hydroxy-acids in the manner described in the experimental part.

The shades (yellow), produced by the leuco-compounds are also lighter than the shade (orange) obtained with the mono-azo-aldehyde; and it is presumably due to the same cause (*i.e.*, too much complexity of the molecule). It may be pointed out here that the leuco-condensation product of 2-hydroxy-*p*-toluic acid does not produce the shade (pink) like that of its condensation product with the dialdehyde. The dyeing property of the oxidized condensation product of 2-hydroxy-*m*-toluic acid with the monoaldehyde almost resembles that of the corresponding compound of phenetole-azo-benzaldehyde-sulphonic acid obtained by Green and Sen (*loc. cit.*) but the shade of the corresponding compound (containing two triphenylcarbinol groups) from the dialdehyde is slightly deeper (blue), whereas the introduction of an additional azo-group makes the colour lighter (Sen and Sett, *loc. cit.*) The same peculiarity, *i.e.*, feeble dyeing property has also been observed in the oxidised condensation product of mono-azo-aldehyde and 2-hydroxy-*p*-toluic acid, which produces on wool a light chocolate shade. This fully confirms the observation that the change in the position of CH_3-group in the molecule has a very marked effect on the dyeing property.

Experimental.

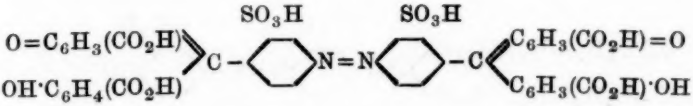
Dyes from Azobenzaldehyde-sulphonic Acid.

Condensation product with salicylic acid (Azodihydroxydicarboxytriphenylmethane-sulphonic acid) :



A mixture of the azo-aldehyde (3·3 g.) and salicylic acid (4·2 g.) was stirred with concentrated sulphuric acid (*d* 1·84, 15 c.c.) for 20 to 30 minutes, when it became pasty and very hot. The mixture is allowed to remain overnight at the room temperature and poured into powdered ice, the precipitate is filtered and washed with a little cold water acidulated with hydrochloric acid. It is finally dissolved in hot water (170 c.c.) and reprecipitated with concentrated hydrochloric acid ; yellow microscopic powder, very soluble in cold water and can easily be precipitated by hydrochloric acid ; dyes wool a yellow shade from an acid bath and on after-chroming the colour of the 3% dyed wool changes to violet-black. (Found : N, 3·22 ; S, 7·10. $C_{42}H_{30}O_{18}N_2S_2$ requires N, 3·06 ; S, 7·00 per cent.)

Oxidation product of the above compound.—

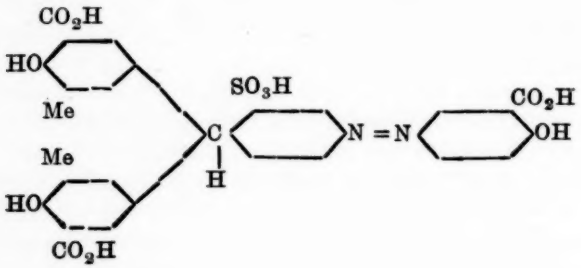


The azo-aldehyde (3·3 g.) is condensed with salicylic acid (4·2 g.) by means of sulphuric acid (15 c.c.). To the sulphuric acid solution of the leuco-compound a solution of nitrosyl sulphate is directly added and the oxidation completed by slowly warming the mixture to 50° for about three hours. The solution is then poured into iced water (110 c.c.), the precipitate is filtered off and washed with acidified water. It is finally dissolved in hot water (160 c. c.) and reprecipitated by hydrochloric acid; red micro-crystalline powder,

soluble in cold water (red solution); dyes wool a red shade. (Found: N, 2·98; S, 7·30. $C_{42}H_{26}O_{18}N_2S_2$ requires N, 3·08; S, 7·03 per cent.).

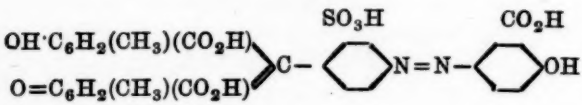
Dyes from Salicylazobenzaldehyde-sulphonic Acid.

Condensation product with cresotinic acid (COOH: OH: CH_3: 1: 2: 3) (*Salicylazodihydroxydimethyldicarboxytriphenylmethane sulphonic acid*).



The condensation is effected in the manner described before; reddish-orange powder, soluble in cold water (yellow solution); dyes wool a yellow shade and on after-chroming a striking series of changes take place and the colour changes finally to black. (Found: N, 4·32. $C_{30}H_{24}O_{12}N_2S$ requires N, 4·42 per cent.)

Oxidation product.—



The oxidation is effected with nitrosyl sulphate; red powder, readily soluble in cold water giving a red solution; dyes wool a red shade. (Found: N, 4·27. $C_{30}H_{22}O_{12}N_2S$ requires N, 4·40 per cent.)

Other azotriphenylmethane dyes from azobenzaldehyde-sulphonic acid and from salicylazobenzaldehyde-sulphonic acid are listed in the following table.

Summary.

(1) In the case of leuco-azotriphenylmethane dyes, the shades (yellow) on wool are lighter than the shades (orange) produced on wool by the aldehydes; this may be attributed to too much complexity of the molecule.

(2) In the case of azotriphenylcarbinol dyes, the depth of shade produced on wool seems to be slightly increased by an addition of a triphenylcarbinol group.

(3) The CH_3-group in the *meta*-position to the OH-group has a remarkable effect in decreasing the intensity of colour and also the dyeing properties of azotriphenylcarbinol dyes.

(4) The influence of an additional OH-group in the *para*-position to the azo-group is practically nil.

TABLE I.

Formulae.	Preparation.	Analysis. Found %	Calc. %	Shade on wool.	Properties.
$C_{40}H_{32}O_{12}N_2S_2$ (leuco-base)	The azoaldehyde-sulphonic acid + cresotinic acid (COOH : OH : CH_3 : 1 : 2 :3) + conc. H_2SO_4.	N, 3·00 S, 6·71	N, 2·89 S, 6·60	Light pink, black on after-chroming.	Reddish-orange powder, easily soluble in water, can be precipitated with HCl.
Oxidation product— $C_{40}H_{30}O_{12}N_2S_2$	By oxidation with nitrosyl sulphate.	N, 2·81 S, 6·81	N, 2·90 S, 6·63	Deep red (bluish).	Dark red powder.
$C_{40}H_{32}O_{16}N_2S_2$ (leuco-base)	The azoaldehyde-sulphonic acid + cresotinic acid (COOH : OH : CH_3 : 1 : 2 : 4) + conc. H_2SO_4.	N, 2·80 S, 6·82	N, 2·89 S, 6·60	Yellow, black on after-chroming.	Yellow powder, sparingly soluble in cold water.
Oxidation product— $C_{40}H_{30}O_{16}N_2S_2$	By oxidation with nitrosyl sulphate.	N, 2·98 S, 6·90	N, 2·90 S, 6·63	Light chocolate.	Reddish-brown powder, readily soluble in water.
$C_{30}H_{24}O_{12}N_2S$ (leuco-base).	Salicylazobenzaldehyde-sulphonic acid + cresotinic acid (COOH : OH : CH_3 : 1 : 2 : 4) + conc. H_2SO_4.	N, 4·36	N, 4·42	Yellow, black on after-chroming.	Yellow powder, soluble in cold water.
Oxidation product— $C_{30}H_{22}O_{12}N_2S$	By oxidation with nitrosyl sulphate.	N, 4·47	N, 4·40	Light chocolate.	Reddish-brown powder, soluble in cold water.

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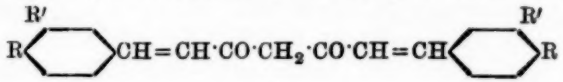
A New Synthesis of Dicinnamoylmethane.

By Krishnasami Venkataraman.

The similarity of the vinyl group to phenyl in some of its reactions and in the properties of the corresponding derivatives was noticed by Norris and Couch (*J. Amer. Chem. Soc.*, 1920, **42**, 2329), who prepared vinyl phenyl ketone by the condensation of benzoyl chloride with ethylene in presence of aluminium chloride. A similar synthesis of benzylidene acetone was achieved a little earlier (Langlois, *Comp. rend.*, 1919, **168**, 1052), the reactants being styrene and acetyl chloride and the condensing agent stannic chloride. Such a method offers an attractive synthesis of dicinnamoylmethane (I, R,R′ = H) and its derivatives, such as curcumin (I, R = OH, R′ = OMe). The process has actually been found feasible, the interaction of malonyl chloride with two molecules of styrene and stannic chloride yielding a small amount of dicinnamoylmethane. The desired substance was isolated from much resinous matter by means of its copper derivative. Dicinnamoylmethane and curcumin have both been previously synthesised (Lampe and Milobedzka, *Ber.*, 1913, **46**, 2235; Lampe, *Ber.*, 1918, **51**, 1347) employing acetoacetic ester.



(I)

Malonyl chloride and bromide have been little exploited for synthetical purposes. Fleicher, Hittel and Wolf (*Ber.*, 1920, **53**, 1847) have observed that malonyl bromide gave better results than the chloride in the preparation of indandiones by its action on acenaphthene. They prepared the bromide for the first time by passing hydrogen bromide through malonyl chloride and fractionating the product. In the present work malonyl bromide has been made by treating the acid with thionyl bromide (Mayes and Partington, *J. Chem. Soc.*, 1926, **129**, 2594). The reaction was tried under widely varying conditions, with and without solvents. In every case considerable decomposition of the thionyl bromide was noticed, followed by separation of pure sulphur as long well-defined needles.

The best yield was obtained by treatment of carefully dried malonic acid with a large excess of thionyl bromide at 100 mm. pressure on the water-bath during two hours and fractionation of the mixture in *vacuo*.

It was found that the replacement of malonyl chloride by bromide in the preparation of dicinnamoylmethane affected the yield but little.

Experimental.

Dicinnamoylmethane.—The reaction was carried out in a three-necked flask fitted with a mechanical stirrer, a separating funnel and a condenser carrying a calcium chloride tube. To a solution of styrene ([" Organic Syntheses," VIII, p. 84], 6 g.) and malonyl chloride ([McMaster and Ahman, *J. Amer. Chem. Soc.*, 1928, **50**, 146], 4 g.) in dry redistilled carbon disulphide (20 g.) cooled in ice, a solution of freshly distilled stannic chloride (14 g.) in carbon disulphide (14 g.) was added drop by drop during one hour. Stirring was continued at room temperature for three hours. A dark red oil had then separated. Crushed ice and dilute hydrochloric acid were then introduced and the whole vigorously shaken. The mixture was extracted with ether, the ether extract washed with water until neutral and the ether removed. On steam-distilling the residue in order to remove any unchanged styrene and cooling, the oily mass solidified and was collected and dried. The powdered material was then refluxed with diethylaniline for an hour, cooled, treated with excess of dilute hydrochloric acid and the whole extracted with ether. The extract was washed with water and mechanically shaken with saturated aqueous copper acetate solution for a few hours. The bulky bluish-green precipitate which had separated was collected, decomposed with dilute sulphuric acid and the diketone taken up with ether. The product obtained from the washed and dried ether extract was apparently a mixture, but on extraction in a Soxhlet with low-boiling petroleum ether led to a homogeneous, crystalline substance, which was collected and recrystallised from dilute alcohol. The dark yellow needles (0·27 g.), m. p. 144°, corresponded in every particular (fluorescence with concentrated sulphuric acid, precipitate with copper acetate solution, colouration with ferric chloride and dye-trial on unmordanted wool) with the dicinnamoylmethane of Lampe and Milobedzka (*loc. cit.*). (Found: C, 82·3; H, 5·9. Calc. C, 82·6; H, 5·8 per cent.)

Malonyl bromide.—When malonic acid was treated with thionyl bromide at atmospheric pressure on the water-bath, it was found that little malonic acid went into solution, while the thionyl bromide decomposed rapidly with evolution of sulphur dioxide, hydrogen bromide and bromine. Various solvents were then tried, but fractionation of the product led to poor yields of malonyl dibromide. In several experiments, a bright orange liquid (which solidified partly on standing) was obtained at 110-120°/10 mm; its bromine value corresponded to that of malonyl monobromide (Found: Br, 34·9. $C_3H_3O_3Br$ requires Br, 34·8 per cent.): no reference to this substance is found in the literature. One typical experiment using ether as solvent may be described. Malonic acid (10 g.), thionyl bromide (60 g.) and dry ether (50 c.c.) were mixed; there was a vigorous reaction and after two hours separation into two layers was noticed—a pale-yellow fluorescent layer and a deep-red lower layer. In addition there were long stout needles, which were collected and identified as sulphur. A little of the top layer was pipetted out and the bromine estimated. (Found: Br, 39·3. $C_3H_3O_3Br$ requires Br, 34·8. $C_3H_2O_2Br_2$ requires Br, 69·6 per cent.) More thionyl bromide (5 c.c.) was added; vigorous reaction again took place and a clear homogeneous solution was obtained. After warming on the water-bath for two hours under reflux, the ether was removed and the residue fractionated at 9 mm. pressure. The following fractions were collected and the bromine value of each was determined.

Boiling point.	Percentage of bromine.
40-50°	50·5
50-55°	69·2
55-80°	25·2
80-95°	31·5
95-105°	34·5

Of the fraction 50-55°, which was obviously the required dibromide, only 3·5 g. were obtained. A quantitative test for sulphur showed that no appreciable amount was present.

The process finally adopted was to treat carefully dried malonic acid with eight times the weight of thionyl bromide on the water-bath under a reflux, the pressure being maintained at 100 mm. so that the thionyl bromide was kept gently boiling. At the end of two hours, the mixture was distilled in *vacuo*, the fraction 50-55°/9 mm. being collected; yield 30-40 per cent. (Found: Br, 69·8.

$C_3H_2O_2Br_2$ requires Br, 69·6 per cent.) The lower fractions consisting mainly of thionyl bromide were preserved and by redistillation at 100 mm. pressure, a certain amount of thionyl bromide was recovered. The action of thionyl bromide on other organic acids is being studied.

I wish to thank Dr. M. A. Govinda Rau for the preparation of the thionyl bromide and the University of Madras for a Research Fellowship which enabled me to carry out the work.

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Effect of Non-Electrolytes on the Precipitation of Thorium Hydroxide from its Salt Solution in Presence of Alkali.

By A. M. Patel and B. N. Desai.

Dhar (*Kolloid Z.*, 1923, **33**, 193), Mehrotra (*J. Indian Chem. Soc.*, 1927, **4**, 117) and Sen (*ibid.*, 1927, **4**, 131) have studied the peptisation of various metallic hydroxides in presence of sugars in a semi-quantitative way. Kuhn and Pirsch (*Kolloid Z.*, 1925, **36**, 310) have made a detailed study of the peptisation of bismuth hydroxide in presence of several sugars. The inhibition of the precipitation of thorium hydroxide in presence of non-electrolytes when caustic soda solution is added to a salt solution of thorium has not yet been studied. It was, therefore, decided to try the effect of non-electrolytes on the precipitation of thorium hydroxide.

An approximately $N/20$ solution of thorium nitrate was prepared and the amount of thorium per 100 c.c. of the solution was then estimated by precipitating as hydroxide and weighing as thorium oxide. A stock solution of caustic soda was also prepared and standardised against oxalic acid. Glycerol and other non-electrolytes, except urea and cane sugar, used in these experiments were purified by redistillation.

The minimum amount of the non-electrolyte necessary to prevent the appearance of the hydroxide of the metal was determined as follows:—

A known volume of the salt solution was taken in a number of test tubes and mixed with varying amounts of the non-electrolyte. In a number of other sets of test tubes a definite amount of alkali was diluted with the calculated amount of water in order to make the total volume (salt solution + non-electrolyte + alkali + water) 25 c.c. The contents of the two sets of test tubes were mixed throughout in a uniform manner. The amounts of the non-electrolyte necessary to prevent the instantaneous appearance of the precipitate of thorium hydroxide were very carefully determined. Experiments were repeated twice and the mean value was taken in

all the cases. The amount of alkali added was greater than what would have been required for the complete precipitation of the hydroxide. The non-electrolytes tried were cane sugar, glycerol acetone, methyl, ethyl and *iso*propyl alcohols and urea. It was found that only cane sugar and glycerol prevented the appearance of the hydroxide.

Effect of the Concentration of the Salt Solution.

Table I contains the results which show the effect of the addition of different amounts of the salt on the inhibition of the precipitation of its hydroxide in presence of cane sugar and glycerol.

TABLE I.

Total volume = 25 c.c. NaOH = 0·6 millimole.

Thorium nitrate (in millimoles).	Cane sugar sufficient to prevent precipitation. (in millimoles).	Glycerol sufficient to prevent precipitation. (in millimoles).
0·00768	1·24	13·7
0·01536	1 64	28 77
0·02304	3·25	71·36
0·03072	5·84	120·83
0·03840	9·62	178·62
0·04608	13·75	—

It is seen from the table that cane sugar is a better inhibiting agent than glycerol. The inhibition of the precipitation of the metallic hydroxide is due to the adsorption of the non-electrolyte and the greater the adsorption of a non-electrolyte, the greater should be its inhibitive power. The fact that the alcohols do not inhibit the precipitation of the hydroxide even when added in large amounts leads one to postulate that the number of hydroxyl groups in the non-electrolyte has something to do with the inhibition of the precipitation of the hydroxide. This view is supported by the results because cane sugar acts is a better inhibiting agent than glycerol due to its having eight OH-groups. The effect of alcohols was negligible because they contain only one OH-group. Urea and acetone have no OH-groups and, therefore, they could not act as inhibiting agents.

According to Graham, the solutions which are formed by the addition of caustic soda to a salt solution of copper or iron in presence of sugar, contain the sucrates of copper and iron. If a definite chemical compound is formed the ratio C_m/C_n should be constant (C_m and C_n are the concentrations in millimoles of the metallic hydroxide and the non-electrolyte respectively). Table II gives the values of the above ratio.

TABLE II.

Amount of salt (in millimole).	Sugar. C_m/C_n.	Glycerol. C_m/C_n.
0·00768	0·00620	0·00056
0·01536	0·00936	0·00530
0·02304	0·00709	0·00032
0·03072	0·00526	0·00025
0·03840	0·00400	0·00022
0·04608	0·00335	—

The value of the ratio C_m/C_n does not remain constant. It first increases and then decreases throughout with an increase in the concentration of the salt solution. The fact that the value of the ratio C_m/C_n is not constant is distinctly in favour of the non-existence of any definite compound of thorium and the non-electrolytes.

Effect of Volume.

Tables III and IV give an idea about the effect of volume change on the amounts of sugar required to prevent precipitation of thorium hydroxide when caustic soda solution is added to a solution of thorium nitrate of different concentrations.

TABLE III.

NaOH=0·6 millimole.

Amount of salt (in millimoles).	Vols. of cane-sugar soln. necessary to prevent precipitation.	
	15 c.c.	25 c.c.
0·00768	1·25	1·24
0·01536	3·15	1·64
0·02304	4·33	3·25
0·03072	7·45	5·84
0·03840	10·73	9·62

TABLE IV.

NaOH = 0·6 millimole.

Amount of salt (in millimoles).	Cane sugar necessary to prevent precipitation (in millimoles).					
	12	15	20	25	30	35 c.c.
0·01536	2·20	2·15	1·84	1·64	1·48	1·10

From Table III it is seen that the amount of sugar required to inhibit the precipitation of hydroxide from the salt solution of a definite concentration in presence of a fixed amount of caustic soda varies with a change in the total volume of the system. Table IV shows that although the amounts of the metal ion and the alkali remain the same, the amount of sugar decreases with an increase in dilution of the system. This volume-effect can be explained in the following manner:—

At a smaller dilution the distances between the individual particles will be smaller than what they will be at a greater dilution and therefore the chances of collisions between the particles will be greater in the former than in the latter. Hence a greater amount of sugar will be required to inhibit the precipitation of the hydroxide at smaller dilutions. Moreover, water itself will act as a peptising agent at greater dilutions and, therefore, the particles will be disintegrated into finer ones thus making the whole system clearer than what it will be at smaller dilutions. This effect will also partly explain why smaller amounts of sugar are required to inhibit the precipitation of a particular amount of the hydroxide at higher dilutions.

The above results can also be explained on the basis of the fact that adsorption is greater from a dilute solution than from a concentrated one. The adsorption of the non-electrolyte being greater from a dilute solution than from the concentrated one less of the non-electrolyte will be required to inhibit the precipitation of the hydroxide in the former case than in the latter.

Amount of Alkali.

It was observed in the preliminary experiments that the amount of sugar or glycerol necessary to prevent the appearance of the hydroxide depended upon the amount of the alkali present in the system although the amount of the metal ion was kept constant. Some experiments were, therefore, tried to investigate this effect. The results of these experiments are given in Table V.

TABLE V.

Total volume = 25 c.c.

Amount of salt (in millimoles).	Cane sugar required to prevent the precipitation of hydroxide (in millimoles). Amount of NaOH in millimoles.					
	0·1	0·2	0·3	0·4	0·5	0·6
0·00768	15·1	1·52	1·24	1·24	1·24	1·24
0·01536	—	5·52	4·25	3·15	2·65	1·65
0·02304	—	15·10	9·82	7·21	5·70	4·20
0·03702	—	19·00	15·31	10·82	8·30	5·85

	Glycerol required to prevent the precipitation of hydroxide (in millimoles). Amount of NaOH in millimoles.					
	0·1	0·2	0·3	0·4	0·5	0·6
0·00768	3·10	2·12	1·41	1 0	1·0	1·0
0·01536	—	5·51	3·82	2·52	1·91	1·71
0·02304	—	20·10	15·12	11·60	8·88	6·31

It will be seen from Table V that when the amount of the metal ion is small the decrease in the amount of alkali is not continuous but soon reaches a minimum value which does not decrease further with any more increase in the amount of the alkali (as far as the maximum amount of the alkali tried in this experiment is concerned). This, however, is not found to be the case with higher concentrations of the metal ion. Although the precipitation of thorium hydroxide from a solution containing 0·03072 millimole of thorium nitrate could be prevented by the addition of 15·1 millimoles of cane sugar in the presence of 0·3 millimole of caustic soda, 19 millimoles of cane sugar were found to be insufficient for the purpose in the presence of 0·2 millimole of alkali. These results are in line with those obtained by Mehrotra (*loc. cit.*) and may be explained on the basis of the view that the non-electrolyte inhibits the precipitation of metallic hydroxide from its salt solution only in the presence of an excess of the alkali. It will thus be seen that neither cane sugar nor glycerol can inhibit the precipitation of the metallic hydroxide by itself in the

absence of an excess of the alkali. The fact that alcohols could not inhibit the precipitation of the hydroxide from its salt solution and that even sugar and glycerol could do so only in the presence of an excess of the alkali supports the conclusion arrived at in another paper ("Relation between purity of thorium hydroxide and its sensitisation by electrolytes," in course of publication) in that as these non-electrolytes coagulate the thorium hydroxide sol they should not be able to peptise it.

The fact that in the presence of increasing amounts of the alkali less and less amounts of the non-electrolyte are required to prevent the precipitation of a colloid can be explained on the ground that a greater amount of the alkali will exert a greater stabilising influence on the colloid and hence the amount of a non-electrolyte required to inhibit the precipitation of the metallic hydroxide will be less.

Summary.

1. The inhibition of the precipitation of thorium hydroxide from the solution of thorium nitrate in the presence of sugar, glycerol, urea, acetone, and methyl ethyl, and *iso*propyl alcohols when sodium hydroxide is added to it has been studied.

2. It is observed that of the above non-electrolytes only cane sugar and glycerol can inhibit the precipitation of the hydroxide and that the former is more effective in its action than the latter.

3. The amount of sugar or glycerol necessary to prevent the precipitation of the hydroxide, other conditions being same, is found to (*a*) increase with an increase in the amount of metal ion, (*b*) decrease with an increase in the dilution of the system—colloid + alkali + non-electrolyte + water, and (*c*) decrease with an increase in the amount of sodium hydroxide.

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The Condensation of Ketones with Resorcinol. Part I. Condensation by Addition.

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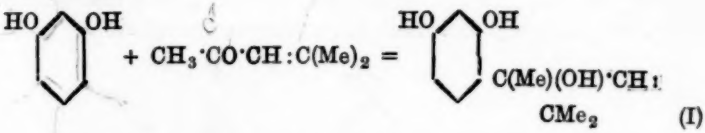
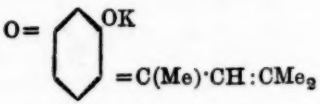
The condensations of ketones with aromatic hydroxy-compounds appear not to have been systematically studied, though a few scattered instances may be found in the chemical literature. The object of the present work was to investigate the condensation of one molecule of a ketone with (*a*) one molecule of the hydroxy-compound (by addition), and (*b*) with two molecules of the hydroxy-compound by the elimination of water. In Part II of this paper the condensation of the second type will be described, those of the first type being dealt with in the present paper.

For the condensation of type (*a*) dilute hydrochloric acid (1 : 1) has been found to be the best condensing agent, the reaction usually taking place at the temperature of the boiling water-bath. In the condensation of acetone with resorcinol, it is interesting to observe that acetone is first converted into mesityl oxide, which subsequently condenses with one molecule of resorcinol giving a colourless product (I), the mechanism of the reaction being thus represented.



(I)

This view is confirmed by the observation that mesityl oxide, when condensed with resorcinol under similar conditions gives a product identical with (I). The product (I) gives a coloured mono-potassium salt having presumably a quinonoid configuration (II),



(II)

a faintly coloured monobenzoyl derivative (quinonoid) and a colourless diacetyl derivative (non-quinonoid) $(AcO)_2C_6H_3{\cdot}C(OH)(CH_3).CH:CMe_2$. The ethylene linkage in the product is

established by the fact that when its alcoholic solution is treated with bromine, a dibromo-addition product is precipitated, which dissolves on further addition of bromine and gives a tribromo-derivative.

Pyrogallol also condenses with acetone under similar conditions, the product $(OH)_3C_6H_2 \cdot C(OH)(CH_3) \cdot CH : C(CH_3)_2$ (III) being obtained.

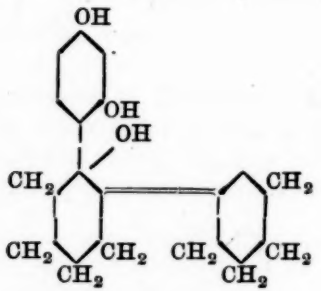
Methyl ethyl ketone and acetophenone under similar conditions are also first transformed into the intermediate products of the mesityl oxide type (not-separated) which then condense with one molecule of resorcinol giving respectively the products

$$(OH)_2C_6H_2 \cdot C(OH)(C_2H_5) \cdot CH : C(C_2H_5)(CH_3) \quad \text{(IV)}$$

and $$(OH)_2C_6H_3 \cdot C(OH)(C_6H_5) \cdot CH : C(CH_3)(C_6H_5) \quad \text{(V)}$$

which, as in the case of product (I), give coloured monopotassium salts, monobenzoyl derivatives and almost colourless diacetyl derivatives.

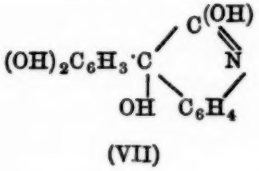
When *cyclo*hexanone and resorcinol were condensed in aqueous solution, two compounds were isolated, one insoluble in alkali which is presumably a polymerisation product of the ketone and the other an alkali soluble product (VI) having the formula $C_{18}H_{24}O_3$ resulting from the condensation of resorcinol and the intermediate ketone. The yield of the condensation product with resorcinol is much better in alcoholic solution than in aqueous solution. The product behaves towards alkali like (I), and gives a monobenzoyl derivative, a diacetyl derivative and a dibromo-derivative.



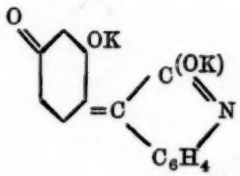
(VI)

From a study of the above compounds it appears that in the case of the simple ketones intermediate compounds of the mesityl oxide type are first formed which then react with resorcinol ; no

condensation with resorcinol taking place in the absence of the formation of such intermediate ketones as in the case of camphor and benzophenone. It is also observed that mesityl oxide reacts with resorcinol readily giving almost theoretical yield whilst acetone reacts after a long time. It is therefore inferred that the grouping —CO—C= in a ketone is essential for this type of condensation, and this view is further confirmed by the fact that such ketones as isatin, benzalacetophenone and benzoylacetone, all readily condense with resorcinol giving almost theoretical yields of the products (VII), (VIII) and (IX) respectively. The condensation products with isatin (VII) and with benzalacetophenone (VIII) give deeply coloured potassium salts (X) and (XI), coloured benzoyl derivatives and almost colourless acetyl derivatives.



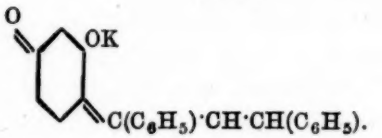
(VII)



(X)

$(OH)_2C_6H_3{\cdot}C(OH)(C_6H_5){\cdot}CH{:}CH(C_6H_5)$

(VIII)



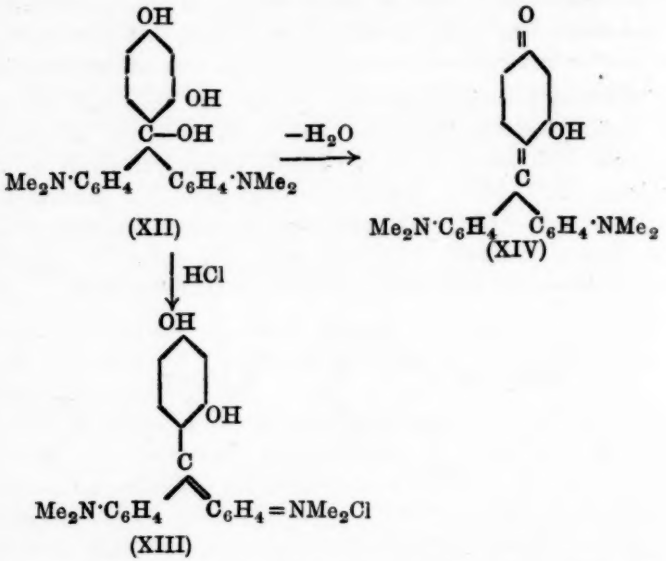
(XI)

$(OH)_2C_6H_3{\cdot}C(OH)(C_6H_5){\cdot}CH{:}C(OH)(CH_3).$

(IX)

This type of condensation by addition does not take place between resorcinol and benzophenone or trihydroxybenzophenone in presence of dilute hydrochloric acid; if, however, the acidic character of the phenyl group is diminished as in Michler's ketone, condensation with resorcinol takes place in molecular proportion by addition, yielding dihydroxymalachite green (XII) which dissolves in

concentrated hydrochloric acid with a pink colour changing to bluish-green on dilution; the hydrochloride (XIII) dyes wool a blue shade.



It is interesting to note that the introduction of two OH-groups in *ortho*- and *para*-positions to the methane carbon atom in malachite green, changes the shade from green to blue.

From a study of the dyeing properties of the compounds described in this paper it is found that where the compound is a derivative of triphenylmethane, the tinctorial character is most marked; in the case of the diphenylmethane derivatives the dyeing property is weakened and it practically disappears when the compound contains only one phenyl nucleus in the molecule as in the condensation products of aliphatic and alicyclic ketones with resorcinol.

Experimental.

The condensations of the ketones with resorcinol were carried out by the following *general method.*

The ketone and resorcinol in molecular proportion were mixed in aqueous or alcoholic solution and the mixture was heated with dilute hydrochloric acid (1 vol. of conc. acid and 1 vol. of water)

on the water-bath for several hours. A solid mass gradually separated, which was filtered and extracted with dilute caustic soda solution. The filtered alkaline solution was acidified with hydrochloric acid. The process was repeated two or three times when the product separated as a micro-crystalline solid. It was filtered, thoroughly washed and recrystallised. The condensation products were invariably soluble in alcohol, benzene, acetone, etc. but insoluble in water.

2:4-*Dihydroxyphenylmethylisobutenylcarbinol* (I).—When a solution of resorcinol (5·5 g.) and acetone (8 c.c.) in 50 c.c. of water was heated with 15 c.c. of dilute hydrochloric acid for 14 hours, as stated above, the product was obtained in 80% yield, which separates from dilute alcohol as a micro-crystalline solid melting at 153°. (Found: C, 69·2; H, 7·9. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7 per cent.).

It is an almost colourless solid, dissolves in dilute caustic soda solution with a deep orange colour, and gives a yellowish-green colour in concentrated sulphuric acid solution. It is soluble in alcohol, benzene, ether and chloroform but insoluble in water.

Potassium Salt (II).—The susbtance was dissolved in a dilute alcoholic solution of pure caustic potash so that an excess of it was present. The excess was filtered off and the coloured solution carefully evaporated to dryness, extracted with small quantities of alcohol and filtered off. The potassium salt is a deeply coloured solid. (Found: K, 17·1. $C_{12}H_{13}O_2K$ requires K, 17·1 per cent.).

Benzoyl Derivative.—The benzoyl compound was obtained as a slightly coloured solid by Schotten-Baumann's method; crystallised from alcohol, it melts at 145°. (Found : C, 77·2 ; H, 6·3. $C_{19}H_{18}O_3$ requires C, 77·6; H, 6·1 per cent.).

Acetyl Derivative.—1·5 G. of the substance were refluxed with 25 c. c. of acetic anhydride and a little zinc dust (1 g.) for two hours. The solution was then poured into 200 c. c. of water and 20 c. c.of alcohol and heated. When the anhydride had completely decomposed the whole was cooled and the precipitate was filtered off, washed with dilute alkali and water and crystallised from alcohol; it was obtained as a colourless solid melting at 162°. (Found: C, 65·5; H, 7·2. $C_{16}H_{20}O_5$ requires C, 65·81; H, 6·95 per cent.).

Dibromo-derivative.—To an alcoholic solution of the carbinol, the required quantity of bromine was added; the percipitate collected, washed, dissolved in alcohol and reprecipitated by water. Crystallised

by slow evaporation of alcoholic solution it melts at 146°-147. (Found : Br, 43·1. $C_{12}H_{16}O_3Br_2$ requires Br, 43·5 per cent.).

Tribromo-derivative.—A slight excess of bromine was added to the alcoholic solution of the carbinol. The precipitate of the dibromo-derivative gradually dissolved. After some time the alcoholic solution was poured into water and the solid precipitate collected, washed and crystallised from dilute alcohol; it melts at 136°. (Found : Br, 53·8. $C_{12}H_{15}O_3Br_3$ requires Br, 53·7 per cent.).

Condensation of Mesityl Oxide with Resorcinol (I).—When a mixture of resorcinol (1·5 g.), water (25 c. c.), mesityl oxide (0·98 g.) and dilute hydrochloric acid (5·7 c. c.) was heated under reflux on a water-bath for 4 hours, the condensation product was obtained after the usual treatment, in almost theoretical yield. It crystallised from dilute alcohol; m.p. 152°-153°. (Found:C, 69·2; H, 7·5 per cent.).

It is found to be identical with the product obtained from resorcinol and acetone, already described.

2:4-*Dihydroxyphenylethylisopentenylcarbinol* (IV).—Resorcinol (3·3 g.), water (45 c.c.), methyl ethyl ketone (6 c. c.) and dilute hydrochloric acid (12 c. c.) on heating for 14 hours gave after usual treatment an almost colourless solid in 80 per cent. yield. It separates from dilute alchol and melts at 118 °. (Found:C, 71·7; H, 8·2. $C_{14}H_{20}O_3$ requires C, 71·8; H, 8·5 per cent.).

It dissolves in alkali with a pink colour and in concentrated sulphuric acid solution gives a yellow shade. In solubility it resembles the compound (I).

Benzoyl Derivative.—Prepared in the usual manner, it crystallised from a mixture of alcohol and benzene as a slightly coloured microcrystalline solid, m. p. 126°. (Found: C, 78·1; H, 6·75. $C_{21}H_{22}O_3$ requires C, 78·3; H, 6·8 per cent.).

Acetyl Deirvative.—Prepared as in the case of compound (I), it was obtained as a colourless solid from dilute alcohol, m. p. 108°. (Found: C, 67·8; H, 7·5. $C_{18}H_{34}O_5$ requires C, 67·5; H, 7·5 per cent.)

2:4:6-*Trihydroxyphenylmethylisobutenylcarbinol* (III).—Pyrogallol (6 g.) in 50 c. c. of water was condensed with acetone (8 c.c.) in presence of dilute hydrochloric acid (15 c. c.) by heating for 15 hours; the product was obtained in about 75-80 per cent. yield. On slow evaporation of an alcoholic solution it is obtained as a slightly coloured solid, which does not melt but decomposes at a high temperature.

(Found: C, 64·0; H, 7·2. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1 per cent.).

In alkaline solution it gives a dark brown colour and it dissolves in concentrated sulphuric acid with a deep orange shade.

2:4-*Dihydorxyphenyl-β-methylstyrylphenylcarbinol* (V).—Acetophenone (6·5 g.) on being condensed with resorcinol (5·5 g.) in alcohol (30 c. c.) and dilute hydrochloric acid (15 c. c.) by heating for 19 hours gave from the alkaline extract of the product after the removal of unchanged aceptophenone by benzene about 40 per cent. yield. On being crystallised by slow evaporation of an alcoholic sclution it was obtained as a dark brown powder melting at 132°-134°. (Found: C, 79·6; H, 6·3. $C_{22}H_{20}O_3$ requires C, 79·6; H, 6·0 per cent.).

It dissolves in alkali with a dark brown colour and in concentrated sulphuric acid with deep orange shade; it is soluble in alcohol, benzene, etc. but insoluble in water.

Potassium Salt.—Prepared in the usual way, it dissolves in water and even in alcohol and is deeply coloured in the solid state. (Found: K, 11·0. $C_{22}H_{17}O_2K$ requires K, 11·0 per cent.).

Benzoyl Derivative.—The free compound on being benzoylated in alkaline solution gave a somewhat coloured solid which crystallised from a mixture of acetone and alcohol melting at 141°. (Found: C,83·1; H, 5·3. $C_{29}H_{22}O_3$ requires C, 83·3; H, 5·3 per cent.).

The *acetyl* derivative is obtained in a manner already described. It crystallised from dilute alcohol and melted at 133°. (Found: C, 75·4; H, 6·3. $C_{26}H_{24}O_5$ requires C, 75·2; H, 6·2 per cent.)

2-cyclo*Hexylidene*-2: 4-*dihydroxyphenyl*-cyclo*hexane*-(1)-*ol* (VI).—On condensing resorcinol (5·5 g.) *cyclo*hexanone (8·5 c. c.) in alcoholic solution with 15 c. c. of dilute hydrochloric acid by heating for 20 hours, the alkali soluble condensation product was obtained in about 80 per cent. yield, which crystallised from dilute alcohol and melts at about 140°. (Found: C, 74·9; H, 8·4. $C_{18}H_{24}O_3$ requires C, 75·0; H, 8·3 per cent.).

It decolourises bromine very easily, gives a brown colour in concentrated sulphuric acid solution and dark brown in alkaline solution. It is slightly yellow in colour in the free state.

The *benzoyl* derivative crystallises from a mixture of benzene and alcohol; m. p. 150°. (Found: C, 80·1; H, 6·9. $C_{25}H_{26}O_3$ requires C, 80·2; H, 6·9 per cent.).

The *acetyl* derivative crystallises from alcohol and benzene;

m. p. 155°. (Found: C, 70·2; H, 7·9. $C_{22}H_{28}O_5$ requires C, 70·2; H, 7·7 per cent.).

Condensation of Isatin and Resorcinol (VII).—On heating a solution of isatin (4·4 g.), resorcinol (3·5 g.) in 150 c.c. of water with 15 c.c. of dilute hydrochloric acid for 5 hours, the product was obtained in almost theoretical yield. It separates from dilute alcohol; it does not melt but decomposes at a high temperature. (Found: C, 65·2; H, 4·2; N, 5·3. $C_{14}H_{11}O_4N$ requires C, 65·4; H, 4·3; N, 5·5 per cent.).

Its solution in alkali is of deep pink colour while in concentrated sulphuric acid it shows an orange-yellow tinge.

The *dipotassium* salt was prepared in the usual way and purified by precipitation with alcohol from concentrated aqueous solution. (Found: K, 24·5. $C_{14}H_7O_3NK_2$ requires K, 24·8 per cent.).

The *dibenzoyl* derivative crystallises from a mixture of acetone and alcohol as a somewhat coloured solid which decomposes at a high temperature. (Found: C, 75·0; H, 4·1. $C_{28}H_{17}O_5N$ requires C, 75·2; H, 3·8 per cent.).

Triacetyl Derivative.—Prepared in the usual way, it crystallises from a mixture of benzene and alcohol and decomposes at a high temperature. (Found: C, 62·6; H, 4·4. $C_{20}H_{17}O_7N$ requires C, 62·6; H, 4·4 per cent.).

2:4-*Dihydroxyphenyl phenylstyrylcarbinol* (VIII).—Benzylidene acetophenone (6·1 g.), resorcinol (3·35 g.) on heating for 12—14 hours and separating slight excess of the ketone, gave about theoretical yield of the condensation product which crystallises from dilute alcohol; m. p. about 190°. (Found: C, 79·7; H, 5·6. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7 per cent.).

The *potassium* salt is a deeply coloured solid soluble in alcohol. (Found: K, 11·8. $C_{21}H_{15}O_2K$ requires K, 11·5 per cent.).

Benzoyl Derivative.—Prepared in the usual way, it crystallises from alcohol-benzene; m. p. 128-130°. (Found: C, 83·3; H, 5·2. $C_{28}H_{20}O_3$ requires C, 83·2; H, 5·0 per cent.).

The *acetyl* derivative is prepared as usual: crystallised from alcohol–benezene; m.p. 153°. (Found: C, 74·3; H, 5·6. $C_{25}H_{22}O_5$ requires C, 74·6; H, 5·5 per cent.).

2:4-*Dihydroxyphenyl phenylacetonylcarbinol* (IX).—When a solution of resorcinol (2·25 g.), benzoylacetone (3 g.) in alcohol was heated with 12 c.c. of dilute hydrochloric acid, an yield of about 80% of the product was obtained after the usual treatment. It crystallises

from dilute alcohol, and does not melt but decomposes at a high temperature. (Found: C, 70·5; H, 5·6. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9 per cent.).

2:4-*Dihydroxyphenyltetramethyldiaminodiphenylcarbinol* or *Dihydroxymalachite Green* (XIV).—Michler's ketone (5 g.) was heated with resorcinol (2·25 g.) in 50 c.c. of dilute hydrochloric acid for 15 hours. The condensation product was obtained in about 20% yield, which is soluble in excess of acid and alkali. After neutralisation of the acid solution with dilute alkali, the product is purified by washing with ether and hot benzene; it melts at about 168°, (Found: N, 7·4. $C_{23}H_{24}O_2N_2$ requires N, 7·8 per cent.).

It is a deep blue powder. In concentrated hydrochloric acid solution it gives a pink shade which changes to bluish-green on dilution. Its solution in concentrated sulphuric acid is orange-red in colour. It is soluble in alcohol and acetone but insoluble in ether, chloroform and benzene.

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Condition of Sparingly Soluble Substances when formed in Presence of a Gel: Silver Bromide, Silver Iodide, and Silver Cyanide in Gelatine.

By A. C. Chatterjee and J. M. Dhar.

In view of the fact that many of the experiments on Liesegang-ring formation in the laboratory are carried out in presence of gels, it is of considerable importance to know exactly the condition in which sparingly soluble substances exist in these gels when freshly formed.

We are of opinion that sparingly soluble substances when formed in gels do exist mainly in the colloidal state; while many believe that they exist in the supersaturated condition. Thus Freundlich states, "The Ag_2CrO_4 (and $Ag_2Cr_2O_7$) formed by the diffusion of silver nitrate into the gelatine containing the bichromate remains in supersaturated solution." The above view of Freundlich is directly based on Ostwald's assumption that supersaturation plays an important part in the formation of Liesegang rings in gels.

We have shown experimentally from electric conductivity measurements that the above view of Freundlich is incorrect and that both silver chromate and chloride in gelatine exist mainly in the colloidal condition.

Recently Bolam and Mackenzie (*Trans. Faraday Soc.*, 1926, **67**, 160) have confirmed the conclusions arrived at previously by Williams and Mackenzie that silver chromate in gelatine exists in the ionic state. But we have already pointed out (*J. Indian Chem. Soc.*, 1928, **5**, 175) from a study of the experimental results of Bolam and Mackenzie that in majority of cases the amount of silver present in the ionic state is approximately only 40% of the total quantity. We are of opinion that the remaining two-thirds of silver which does not exist in the ionic state, remains in a colloidal condition. Hence the measurements of Bolam and Mackenzie are in support of our views.

Moreover, in view of the high protective action of gelatine it is only natural that the sparingly soluble substances when formed in

presence of the above gel should remain in the colloidal condition and not give rise to supersaturated solution. Thus, to quote Freundlich, "in suffciently concentrated solutions of gelatine, it is possible to prevent the separation of practically every precipitate which is difficultly soluble in water and to retain it colloidally dispersed in solution." Svedberg was actually able to prepare colloidal solutions of silver chloride and bromide and Prussian blue by precipitating them in gelatine. Consequently, it is difficult to understand how substances like silver chloride, silver chromate, etc., can remain in the supersaturated condition in gelatine.

An objection may be raised that due to the presence of a viscous medium, the electric conductivities will be greatly reduced and, therefore, the conclusions drawn from them may not be accurate. But Arrhenius proved long ago that the electric conductivities of substances like hydrochloric acid, nitric acid, etc., when set in gelatine are practically the same as in aqueous solutions. Moreover, electric conductivities in all cases are measured in presence of the same viscous medium. Therefore, any change which the conductivities suffer due to the presence of the viscous medium affects all the cases equally, and does not change the final conclusions.

In this paper we have carefully determined the electric conductivities of silver chloride, bromide and cyanide in gelatine. We have also determined the concentrations of the silver ions in the case of the above three salts in gelatine by *E. M. F.* measurements. The experimental results obtained are in complete agreement with the conclusions arrived at in previous papers.

The reason why the above salts of silver are chosen is that these salts are not affected like silver chromate by the hydrogen-ion concentration of the medium, and therefore, the percentage of silver in the ionic condition should be far less than that found by Bolam and Mackenzie with silver chromate. This conclusion of ours has been proved to be correct from the results recorded in this paper.

Experiments were undertaken to find out the electric conductivities of different amounts of silver bromide, silver iodide and silver cyanide in gelatine at 20°. Nelson's "A_2-gelatine" was used and it was purified by the method of J. Loeb (*J. Gen. Physiol.*, 1918, **1**, 235) to give an ash-free gelatine, which has been employed in all the experiments described in this paper.

As the sparingly soluble silver salts were obtained by the addition of equivalent quantities of silver nitrate and potassium salt of the corresponding acid, in every case, an equivalent amount of potassium nitrate was also produced. In order to ascertain the conductivity of the sparingly silver salt alone, the conductivity of an equivalent concentration of potassium nitrate in gelatine was determined under identical conditions.

A typical result of the conductivity measurements obtained with silver bromide is shown in Table I. Exactly similar results were obtained with other concentrations of the sparingly soluble salt. The results obtained are summarised in Table II. From the conductivity measurements given in Table I, the conductivity of silver bromide as determined by experiment can be ascertained by simply subtracting the conductivity of potassium nitrate from that of the mixture of potassium bromide and silver nitrate. If it is assumed that the whole of AgBr remains in the ionic condition and not in the colloidal state, then its conductivity should be equal to the sum of the conductivities of potassium bromide and silver nitrate *less* the conductivity of potassium nitrate alone. Table II contains results calculated on the basis of the above considerations.

Electric conductivity of AgBr *in gelatine.*

TABLE I.

Temperature at which the experiments were performed.	...	20°.
Concentrations of AgBr, $AgNO_3$, KBr, KNO_3.	...	*N*/800.
Concentration of gelatine solution.	...	0·5 gm. per 100 c.c.
Conductivity of water.	...	$2{\cdot}085 \times 10^{-6}$ mhos.
Conductivity of gelatine.	...	$0{\cdot}518 \times 10^{-4}$,,
Conductivity of gelatine + $AgNO_3$.	...	$1{\cdot}703 \times 10^{-4}$,,
Conductivity of gelatine + KBr.	...	$2{\cdot}000 \times 10^{-4}$,,
Conductivity of gelatine $AgNO_3$ + KBr.	...	$1{\cdot}972 \times 10^{-4}$,,
Conductivity of gelatine + KNO_3.	...	$1{\cdot}992 \times 10^{-4}$,,

TABLE II.

Concentration of AgBr.	Observed conductivity.	Conductivity calc. from exp. results assuming AgBr to be wholly in the ionic state.	Percentage of Ag as ions.
N/800	$-0{\cdot}020 \times 10^{-4}$ mhos.	$1{\cdot}711 \times 10^{-4}$	*nil*
N/400	$-0{\cdot}013 \times 10^{-4}$,,	$2{\cdot}790 \times 10^{-4}$	*nil*
N/200	$0{\cdot}009 \times 10^{-4}$,,	$10{\cdot}343 \times 10^{-4}$	0·8

In the above experiments the conductivity of gelatine is far less than those which were used in experiments recorded in previous papers.

From results recorded in Table II, it is evident that if the whole of the silver bromide were present in the ionic condition, the conductivity observed would have been much greater than the values actually obtained. As a matter of fact, in the majority of cases investigated, the *minus* sign in the column of observed conductivity indicates that the conductivity of a mixture of silver bromide and potassium nitrate is less than that of the latter alone.

Hence the foregoing experimental results lead us to the conclusion that silver bromide formed in gelatine by the interaction of equivalent quantites of silver nitrate and potassium bromide exists mainly in the colloidal state.

Exactly similar experiments were conducted with silver iodide in gelatine. The results obtained are given in Tables III and IV.

Electric conductivity of silver iodide in gelatine.

TABLE III.

Temperature at which the experiments were performed.	20°.
Concentrations of AgI, $AgNO_3$, KI, KNO_3.	$N/800$.
Concentration of gelatine solution.	0·5 gm. per 100 c.c
Conductivity of water.	$2·160 \times 10^{-6}$ mhos.
Conductivity of gelatine.	$0·408 \times 10^{-4}$,,
Conductivity of gelatine + $AgNO_3$.	$1·578 \times 10^{-4}$,,
Conductivity of gelatine + KI.	$1·708 \times 10^{-4}$,,
Conductivity of gelatine + $AgNO_3$ + KI.	$1·956 \times 10^{-4}$,,
Conductivity of gelatine + KNO_3	$1·993 \times 10^{-4}$,,

TABLE IV.

Concentration of AgBr.	Observed conductivity.	Conductivity calc. from exp. results assuming AgBr to be wholly in the ionic state.	Percentage of Ag as ions.
$N/800$	$-0·037 \times 10^{-4}$ mhos.	$0·995 \times 10^{-4}$ mhos.	*Nil*
$N/400$	$-0·103 \times 10^{-4}$,,	$2·197 \times 10^{-4}$,,	,,
$N/200$	$-0·124 \times 10^{-4}$,,	$5·113 \times 10^{-4}$,,	,,
$N/100$	$-0·200 \times 10^{-4}$,,	$10·662 \times 10^{-4}$,,	·2

From the above table it is clear that silver iodide has always a negative value for its observed conductivity. In other words, the conductivity of a mixture of silver iodide and potassium nitrate is always *less* than that of the latter alone in gelatine. This lowering in the conductivity is certainly due to the fact that somehow a portion of potassium nitrate has been removed from the field of action, thereby lowering its effective concentration. This is most probably due to the adsorption of potassium nitrate by silver iodide precipitate during formation.

Exactly similar results have also been obtained with silver cyanide in gelatine. The values obtained are summarised in Tables V and VI.

TABLE V.

Temperature at which the experiments were performed ..	20°.
Concentration of AgCN, $AgNO_3$, KCN, KNO_3 ...	$N/800$.
Concentration of gelatine solution	0·5 gm. in 100 c.c.
Conductivity of water	$2·620 \times 10^{-6}$ mhos.
Conductivity of gelatine	$0·511 \times 10^{-4}$,,
Conductivity of gelatine + $AgNO_3$	$1·707 \times 10^{-4}$,,
Conductivity of gelatine + KCN	$1·250 \times 10^{-4}$,,
Conductivity of gelatine + $AgNO_3$ + KCN	$1·946 \times 10^{-4}$,,
Conductivity of gelatine + KNO_3	$1·940 \times 10^{-4}$,,

TABLE VI.

Concentration of AgCN.	Observed conductivity.	Conductivity calc. from exp. results assuming AgCN to be wholly in the ionic state.	Percentage of Ag as ions.
$N/800$	$0·006 \times 10^{-4}$ mhos.	$0·9683 \times 10^{-4}$ mhos.	0·62
$N/400$	$0·056 \times 10^{-4}$,,	$3·4830 \times 10^{-4}$,,	1·60
$N/200$	$0·066 \times 10^{-4}$,,	$3·4396 \times 10^{-4}$,,	1·92
$N/100$	$0·21 \times 10^{-4}$,,	$8·4480 \times 10^{-4}$,,	2·50

From the above table it will be seen that if silver cyanide were present wholly in the ionic condition, the observed conductivities should have been much greater than the values actually obtained. In no case the percentage of silver cyanide present in the ionic condition is greater than 2·5% as is clear from the values given in the last line of the above table. Hence more than 95% of silver cyanide is present in a state other than ionic. We are of opinion that this major portion of the sparingly soluble salt is in the colloidal state.

Conclusions drawn from the Conductivity Experiments.

From Tables II, IV and VI it will be evident that silver bromide, iodide and cyanide have much less electric conductivities than they should have if they were wholly in the ionic state.

The simultaneous production of an equivalent amount of potassium nitrate and the possibility of its adsorption by the freshly prepared sparingly soluble silver salts investigated during the course of their formation, may affect the observed conductivity of these salts. Hence in all cases the observed conductivity may be slightly less than that which should be found out if there were no adsorption of potassium nitrate and therefore, it might be argued that the evidence brought forward by electric conductivity determinations as to the condition in which the sparingly soluble salts are present when formed in gelatine may not exactly represent the true state, and the percentage of silver present in the ionic state may be increased. But the magnitude of the increase introduced will not be appreciably large in view of the fact that the adsorption of potassium nitrate by sparingly soluble silver salts has been found to be not very great. Mukherjee and Kundu (*J. Indian Chem. Soc.*, 1926, **3**, 335) have determined the adsorption of electrolytes by pure silver iodide, and they are of opinion that of the cations—Ag, K, Ba, Ca and Al,—the order of adsorption is $Ag \geqslant Al > Ba : Ca > K$ or in other words, K is least adsorbed of all the cations investigated. Among the anions investigated the order of adsorption appears to be $Br > NO_3 > Cl > SO_4$.

Beekley and Taylor (*J. Phys. Chem.*, 1925, **29**, 1942) have recently measured by analytical methods the adsorption of ions by precipitated AgI. They have found out the order of adsorption to be benzoate $\geqslant$ acetate > nitrite $\geqslant$ nitrate $\geqslant$ chlorate $\geqslant$ perchlorate.

The authors employed soluble silver salts of the above acids for determining the adsorption, and their results with silver nitrate are given below.

Silver Iodide. Preparation No. 6. Temp. 25°.

M	C_0	C_1	m	a
73·239	0·008058	0·007944	2·874	0·0029
71·129	0·009787	0·000689	2·318	0·0030

where M = the weight of the solution ;

C_0 = the initial concentration in millimoles per gram of soln.;

C_1 = the equilibrium " " " " " " "

m = the weight of silver iodide;

a = the amount of adsorption salt in millimoles per gram of silver iodide.

The amount of adsorption was calculated from the formula,

$$a = \frac{M(C_0 - C_1)}{m}$$

From the above table we have calculated the following results:—

Amount of $AgNO_3$ in one gram of the solution $= 1{\cdot}369 \times 10^{-3}$ g.
Amount of AgI in 80 c.c. $= 2{\cdot}873$ g.
Percentage of adsorption of $AgNO_3$ per gram of AgI $= 0{\cdot}49$.

In our experiments the concentration of potassium nitrate was $8{\cdot}08 \times 10^{-3}$ g. in 80 c.c. of the solution while the amount of silver iodide was never more than 0·0469 g. With this quantity of silver iodide the adsorption of the nitrate should be considerably lower than that found by Beekley and Taylor. Moreover, according to Mukherjee and Kundu the adsorption of potassium nitrate is lower than that of silver nitrate. Hence it can be safely asserted that the quantity of potassium nitrate adsorbed will be considerably less than that of silver nitrate (0·49%) as calculated from Beekley and Taylor's data.

Therefore, the error introduced due to the adsorption of potassium nitrate (which is simultaneously produced) by the silver salts will not be great and the results obtained can be easily taken to give a fairly accurate idea of the state in which these sparingly soluble silver salts do exist when formed in presence of gelatine.

From the above results on the electric conductivity, it can be safely deduced that more than 95% of silver bromide, iodide and cyanide remain in a condition other than ionic in gelatine. We are of opinion that these large quantities of silver salts remain in a colloidal state.

In this connection, it is of interest to note the conclusions arrived at by Bolam in a recent paper (*Trans. Faraday Soc.*, 1924, **24**, 461) that lead iodide in agar remains in a supersaturated condition. As the observed conductivity of lead iodide in agar increases with an increase in the concentration of the salt and can reach a value almost three times that of the initial concentration, it has been assumed that lead

iodide exists in the supersaturated state. This assumption is further strengthened by the observation that the conductivities at higher concentrations of lead iodide in agar are greater than that of a saturated solution of the salt prepared by dissolving a freshly prepared precipitate of lead iodide in conductivity water.

The above simply proves that in concentrated solutions of lead iodide in agar, a part of the salt is in the ionic condition. It does not prove that all or what part of the salt is in the ionic state.

We have emphasised in previous papers that the proper method to know exactly what portion of the sparingly soluble salt remains in the ionic state, is first to find out the conductivity of the salt assuming it to exist wholly as ions, and then to compare this value with the conductivity actually found out by direct experimental determinations. The former value can be calculated from the conductivities of each of the reacting electrolytes, and in this particular example, it is equal to the *sum* of the electric conductivities of lead nitrate and potassium iodide in agar *less* that of potassium nitrate also in agar. Bolam has simply determined the latter values and compared these values among themselves instead of with those calculated on the assumption that the salt exists wholly in the ionic condition.

The following table gives a comparison of the two sets of values as found by Bolam himself. The conductivities of lead iodide ($K_1 - K_2$) as determined by direct experiments have been taken from the last column of Tables III and IV of Bolam's paper, whilst the values for the conductivities of lead nitrate, potassium iodide and potassium nitrate have been calculated from the observations recorded in Table VI of the above paper.

TABLE VII.

Electric conductivities of PbI_2 *of such concentrations as remain colourless in agar.*

1	2	3	4	5	6	7	8	9
Milli-equivalents.	$Pb(NO_3)_2$	KI	KNO_3 K_2	$Pb(NO_3)_2$ + KI K_1	PbI_2 observed $K_1 - K_2$	PbI_2 calculated wholly as ions (2+3)−4.	Difference (7−6)	Percentage of PbI_2 present in the ionic state.
3·178	288	431	412	617	305	307	2	99·3
7·911	769	1066	1020	1723	703	815	112	86
12·62	1233	1682	1612	2496	885	1303	418	67
				2429	817	1303	486	62
				2347	735	1303	568	56
				2306	684	1303	619	52

From the above table it is clear that the percentage of lead iodide in the ionic state decreases as the concentration of lead iodide increases—a conclusion which is exactly opposite to that of Bolam deduced from a consideration of the values given in column 7 only of the above table. Though the percentage of lead iodide in the ionic state appreciably decreases, it is certainly more than what we should ordinarily get. In our opinion, the large value of $K_1 - K_2$ is due to the presence of sulphate ions in agar solution used by Bolam. The sulphate removes a part of lead nitrate as lead sulphate, and thus lowers its conductivity considerably. The effect of this is to decrease the values given in column 7. On the other hand, it increases the values given in column 6 due to a secondary reaction proceeding simultaneously as indicated below:—

(1) $Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3$ (usual)

(2) $Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$ (secondary)

Due to this secondary reaction, a part of the lead nitrate is used up in removing the sulphate leaving a portion of potassium iodide unused, when the latter is mixed with lead nitrate to produce lead iodide. The result of this is that the values in column 5 give us the conductivities of a mixture of lead iodide, potassium nitrate, nitric acid, potassium iodide and lead sulphate and not of lead iodide and potassium nitrate alone as was assumed by Bolam. The presence of unused potassium iodide in place of lead iodide gives us higher values in column 5. Hence the values recorded in column 6 are correspondingly high. With pure agar, we should expect to get much lower values for lead iodide in the ionic state than those recorded here from Bolam's observations.

The second evidence brought forward by Bolam is that the conductivity of a mixture of lead nitrate and potassium iodide remains constant up to a certain concentration and lead iodide in these mixtures exists largely as free ions.

From Bolam's own observations, we have calculated a relation between the concentration of lead iodide in agar and the diminution in conductivity with time. The results obtained are given in Table A. In order to compare these with the diminutions observed in case of lead iodide in conductivity water, Table B has been calculated from the results recorded in Table V of Bolam.

TABLE A.

Conc. of PbI_2 in agar.	Time.	Diminution.
3·173-10·67		No diminution with time.
10·87	23 hrs.	29
	*23 ,,	70
11·58	25 ,,	125
	*24 ,,	107
12·62	4 ,,	150
	*25 ,,	133

TABLE B.

Conc. of PbI_2 in H_2O.	Time.	Diminution.
3·173-3·821		No diminution.
4·008	24 hrs.	1
5·010	39 min.	16
	·24 hrs.	83
	*24 hrs.	77
	·24 hrs.	84·7
	*24 hrs.	88·5

* Separate experiments.

From the above it is clear that even in case of lead iodide in water there is a perceptible decrease in the electric conductivity. If this decrease is negligible and it can be assumed that lead iodide in water remains in the ionic state, there seems to be no justification not to regard lead iodide in agar also to be in the same state, as the diminution in the latter case is proportional to its concentration. Hence, Bolam's assumption that lead iodide in agar (in those solutions that have a constant conductivity) remains in the ionic condition, does not carry conviction in the light of the above observations. The conductivity remains constant up to $C=10·67$. Beyond this the diminution is perceptible. If it is assumed that lead iodide up to $C=10·67$ remains in the ionic state, beyond this concentration it can by no means be assumed to be so. One interesting point that arises from this assumption is the nature of the condition in which lead iodide remains between $C=10·67$ and $C=12·62$, the limit at which lead iodide immediately turns pale yellow.

In our opinion the constant conductivity at lower concentrations of lead iodide is not due to the salt being in the ionic state but is due to the high protective action of agar at these concentrations; on the other hand, at higher concentrations of lead iodide the decrease in conductivity may be due to the gradual adsorption of potassium nitrate by particles of lead iodide formed on standing due to lesser protective action of agar.

Hence from a more critical study of Bolam's own observations, it is difficult to support the conclusions arrived at by him.

In order to compare the results obtained from the electric conductivity data, we have measured the amount of silver present as ions in the sparingly soluble silver salts by *E.M.F.* determinations. The same preparation of gelatine and of an equal concentration as used in the conductivity experiments, has been employed. The *E.M.F.* has been determined by measuring the *P.D.* of a cell of the type given below:

Ag	$AgNO_3$ N/10	KNO_3 normal	Silver salt in gelatine	Ag

From the value of the *E.M.F.*, the concentration of silver ions has been calculated. The results obtained are given below.

Experiments with silver bromide.

TABLE VIII.

Concentration of gelatine = 0·5 per cent. Temperature = 20°.

No.	Conc. of AgBr : normality × 10^6	Conc. of Ag present as ions : normality × 10^6	Percentage of Ag as ions.
1.	10090	1·19	0·0119
2.	5000	1·156	0·0231
3.	2500	1·135	0·0454
4.	1250	1·125	0·09
5.	625	1·114	0·19

From the above table it is clear that the amount of silver present in the ionic condition is never more than 0·2 per cent. even when the concentration of silver bromide is considerably varied. Moreover the amount of silver present in the ionic condition almost proportionately increases with the decrease in the concentration of silver bromide. Though the quantity of silver as ions is so small in the above cases, it is about 1·4 times the quantity soluble in pure water. From the foregoing experiments, if is absolutely clear that almost cent. per cent. of AgBr exists in a condition other than ionic, and we are strongly of opinion that this large amount of silver is in the colloidal state.

Experiments with silver iodide.

Similar experiments were performed with silver iodide. The results obtained are given below.

TABLE IX.

Concentration of gelatine = 0·5 per cent. Temperature = 20°.

No.	Conc. of AgI : normality × 10^6.	Conc. of Ag present as ions : normality × 10^6.	Percentage of Ag as ions.
1.	4000	8·38	0·21
2.	3000	7·22	0·24
3	2000	5·76	0·29
4	1000	3·67	0·37

In this case, the amount of silver present in the ionic condition is less than 0·5 per cent. Here also, we find that almost all the silver salt is in a condition other than ionic. In the conductivity experiments, we always obtained a *negative* value for the conductivity of silver iodide, which indicated that almost all the salt is in a colloidal state, a conclusion that is completely corroborated by results obtained from *E.M.F.* measurements as given in the above table.

The results obtained with silver cyanide are given below.

Experiments with silver cyanide.

TABLE X.

Concentration of gelatine = 0·5 per cent. Temperature = 20°.

No.	Conc. of AgCN : normality × 10^6.	Conc. of Ag present as ions : normality × 10^6.	Percentage of Ag as ions.
1.	10000	16·52	0·165
2.	5000	8·15	0·063
3.	2500	4·86	0·194
4.	1250	3·65	0·292
5.	625	3·27	0·523

From the above table, it is clear that the amount of silver in the ionic condition is never more than 1 per cent. whereas from results on electric conductivity experiments, the percentage of silver in the

ionic condition is with certain concentration of silver bromide as high as 2·5.

The following table gives a comparison of the results obtained with silver cyanide by both the methods.

TABLE XI.

No.	Conc. of AgCN : normality × 10^6.	Percentage of Ag present in the ionic condition. From electric conductivity data.	From *E.M.F.* measurements.
1.	10000	2·5	0·165
2.	5000	1·95	0·63
3.	2500	1·6	0·194
4.	1250	0·62	0·292

The following results were obtained when silver chloride was the sparingly soluble salt used.

TABLE XII.

Concentration of gelatine = 0·5 per cent. Temperature = 20°.

No.	Conc. of AgCl : normality × 10^6.	Conc. of Ag present as ions : normality × 10^6.	Percentage of Ag as ions.
1.	10000	259	2·59
2.	5000	37·2	0·744
3.	2500	3·9	0·156
4.	625	3·15	0·504

The amount of silver present in the ionic condition is never more than 3 per cent.—a conclusion which was arrived at while measuring the electric conductivity of AgCl in gelatine. (*J. Indian Chem. Soc.*, 1928, **5**, 175).

Summary.

1. Measurements of electric conductivities of silver chloride bromide and iodide of different concentrations in gelatine prove that the observed conductivity is much less than the conductivity calculated on the assumption that the above silver salts exist as ions in the gel. Exactly similar results were obtained with silver chromate and silver chloride in gelatine previously.

2. From the electric conductivity results it has been found out that in the case of silver chloride and iodide the conductivity of a mixture of the silver salt and potassium nitrate is *less* than the conductivity of potassium nitrate alone, while in the case of silver cyanide the amount of silver present in the ionic condition never exceeded 2·5 per cent.

3. From the results obtained by *E.M.F.* determinations, it has been found out that in the case of silver chloride, bromide, iodide and cyanide the amount of silver present in the ionic condition never exceeded more than 3 per cent. even when the concentration of the sparingly soluble silver salts was considerably varied. We are of opinion that the rest 97 per cent. of Ag exists in a colloidal condition.

4. The hydrogen-ion present in gelatine (p_H 5·0) cannot dissolve the sparingly soluble silver salts examined, and hence in the cases of silver bromide, iodide and cyanide the amount of free silver ions present with these salts is much less than in the case of silver chromate in gelatine.

In conclusion, our thanks are due to Prof. P. S. MacMahon for providing facilities to carry on the above work. We are also thankful to Dr. N. R. Dhar for his interest in the work. One of us (J.M.D.) is indebted to the authorities of the Lucknow University for kindly granting him a research fellowship that has enabled him to participate in the above investigation.

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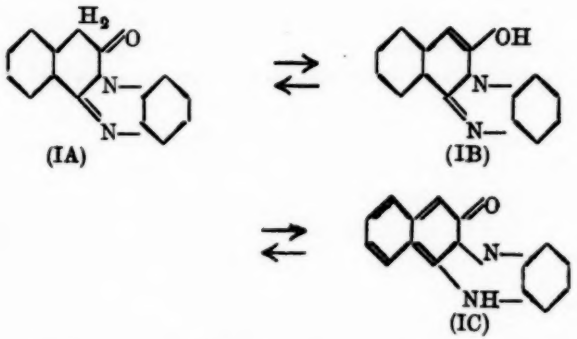
Colour of Complex-Diazoles. Part III. Reduced Pyrrole-Iminazole Compounds.

By Mangesh V. Betrabet and Gopâl Chandra Chakravarti.

In Part II of this series it has been pointed out by Chakravarti and Sen-Gupta (*J. Indian Chem. Soc.*, 1925, **1**, 330) that iminazoles derived from camphoric anhydride and aromatic diamines which contain reduced pyridine and iminazole rings condensed together in their molecules are colourless. Bistrzycki and Fässler (*Helv. Chim. Acta*, 1923, **6**, 521), however, found that *o*-phenylene acetyl-1 : 3-benziminazole (IA) containing a partially reduced pyridine-iminazole skeleton was deep greenish-yellow in colour. But, although all of them contain reduced pyridine rings in the molecules, the camphor derivatives cannot be represented by any other alternative formulæ, whereas Bistrzycki and Fässler's compound admits of three different configurations :—

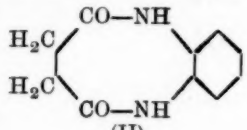


(IA) (IB) (IC)

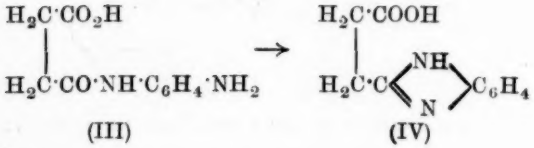
Formula (IC) represents a quinonoid structure and the colour of this compound may be attributed to this property of existing as tautomeric quinonoid and non-quinonoid structures (*cf.* Watson, *Proc. Chem. Soc.*, 1913, **29**, 348; *J. Chem. Soc.*, 1914, **105**, 750). As regards the absence of colour in the camphor-iminazoles, Chakravarti and Sen-Gupta (*loc. cit.*) had suggested that this was not due to any hypsochromic effect of the camphor part of the molecule but might be due to the absence of a kind of unsaturated linkages like the

ortho- or *para*-quinonoid structures. These observations and some results obtained by us during the determination of the absorption spectra of several coloured and colourless complex iminazoles that are in progress in this laboratory for elucidating a relationship between their colour and constitution necessitated the investigation of similar reduced pyrrole and iminazole derivatives.

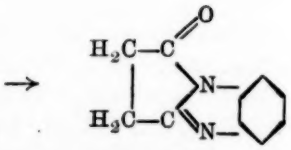
The simplest reduced pyrrole-iminazole was prepared by condensing succinic anhydride with *o*-phenylene diamine. Bistrzycki and Fässler (*loc. cit.*) failed to bring about this condensation. After several trials we found that the reaction could be brought about by following a method employed by Anderlini (*Gazzetta*, 1894, **24**, 140). He appears to have obtained an additive compound $C_6H_4(NH_2)_2$, $C_2H_4O_3$ of m.p. 80° (decomp.) by mixing the anhydride and the diamine in cold benzene solution. This additive compound was supposed to be converted into an eight membered ring-compound *o*-phenylene succinyldi-imide (II), m.p. 237°, on boiling the former either with benzene or absolute alcohol. We, however, could not isolate any additive compound having m.p. 80°, the first product of the reaction being invariably an acid imide, *o*-aminophenyl-amidosuccinic acid (III), m.p. 148-150° (decomp.). The latter was converted into benziminazole-2-propionic acid (IV), m.p. 225-226°, and not into the eight-membered ring-compound (II), by boiling with absolute alcohol.



(II)



(III) (IV)



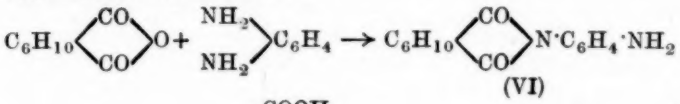
(V)

Thiele and Falk (*Annalen*, 1906, **347**, 112) made a similar observation in the case of an analogous product from phthalic anhydride and

o-phenylene diamine, which was proved to be identical with benziminazole-2-*o*-benzoic acid of Bistrzycki (*Ber.*, 1890, **23**, 1042) and therefore, did not contain an eight membered ring. Moreover, in a recent paper, Phillips (*J. Chem. Soc.*, 1928, 2393) carried out the condensation between succinic acid and *o*-phenylene diamine in the presence of 4*N*-hydrochloric acid and obtained an acid of m.p.225°. We also prepared this compound by Phillips' method and confirmed its identity with our acid (IV) by a mixed melting point. The constitution of the acid (IV) is therefore established. The benziminazole-2-propionic acid (IV) was then converted into (α:β)-dihydroacrylene-1:3-benziminazole (V) by the usual methods.

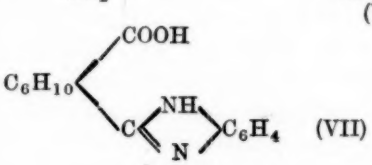
Other reduced pyrrole-iminazoles were prepared by condensing hexahydrophthalic anhydride with aromatic diamines. For this condensation we needed hexahydrophthalic acid in quantity. We found, however, that the existing well-known methods for obtaining this compound (Baeyer, *Annalen*, 1890, **258**, 198; Willstätter and Jaquet, *Ber.*, 1918, **51**, 770) gave very unsatisfactory yields. We, therefore, prepared platinum oxide according to the method of Voorhes and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 1397) and used this catalyst for the reduction of phthalic acid. We further found that the use of 95% alcohol as the solvent facilitates this reduction.

By this method very good yields of hexahydrophthalic acid were obtained. The anhydride of this acid had m.p. 32° corresponding to the *cis*-variety. The anhydride was then condensed with *o*-phenylene, 1:3:4-tolylene and 1:2-naphthylene diamines in absolute alcoholic solutions. The products which were either acid or anils, or usually a mixture of both, were then converted into the condensed iminazoles by the ordinary methods. The reactions in the case of the *o*-phenylene diamine were as follows:—

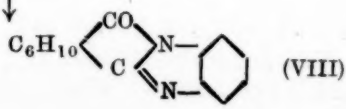


(VI)

and



(VII)



(VIII)

From an analogy with the colourless reduced pyridine-iminazoles prepared by Chakravarti and Sen-Gupta (*loc. cit.*) from camphoric anhydride, it was anticipated that these reduced pyrrole-iminazole derivatives should come out as colourless compounds. This expectation has been realised and the iminazoles described in this paper have been obtained in beautiful colourless crystalline forms.

Experimental.

o-Aminophenylamidosuccinic Acid (III).—Succinic anhydride (5 g.) was suspended in 35 c.c. of hot dry benzene and to this was added *o*-phenylene diamine (5·4 g.) dissolved in 15 c.c. of benzene. The reaction was completed in a few minutes by shaking well, when a white pasty mass was deposited. This was separated and crystallised from alcohol in colourless silky needles, m.p. 148-150°, which are soluble in alkali carbonates, and in dilute acids, and give tests for primary amines. (Found: N, 13·2. $C_{10}H_{12}O_3N_2$ requires N, 13·5 per cent.).

Benziminazole-2-propionic Acid (IV).—*o*-Aminophenylamidosuccinic acid (5 g.) was boiled under reflux for three hours with 50 c.c. of absolute alcohol. The volume of the alcohol was reduced to one-third and allowed to stand when colourless prisms were deposited. They were crystallised from hot water in short colourless prisms which were soluble in alkali carbonates and strong acids; m.p. 225-226°. (Found: N, 14·90. $C_{10}H_{10}O_2N_2$ requires N, 14·74 per cent.). This compound was also prepared by Phillips' method (*loc. cit.*) and the mixed melting point was also 225°.

(α:β)-Dihydroacrylene-1:3-benziminazole (V).—Benziminazole-2-propionic acid (3 g.) was boiled under reflux with excess of acetic anhydride for half an hour. The excess of acetic anhydride was evaporated off. The residue was a sticky blackish mass which was purified by extraction with ether and hot benzene, when it gave a slightly dirty powder. This was dissolved in absolute alcohol and boiled with animal charcoal for two hours and after filtration the alcohol was removed. The residue was crystallised from nitrobenzene in colourless rosettes. From alcohol these come out as colourless silky needles, m.p. 172-175°. The crystals are insoluble in alkalis, but dissolve in concentrated acids. (Found: C, 69·48; H, 4·72; N, 16·43. $C_{10}H_8ON_2$ requires C, 69·76; H, 4·65; N, 16·27 per cent.).

This iminazole is also obtained by heating benziminazole-2-propionic acid at 230° for fifteen minutes and crystallising from alcohol.

Hexahydrophthalic acid.—Phthalic acid (10 g.), freshly precipitated from its sodium salt, was dissolved in 75 c.c. of 95% alcohol and was placed in a pressure resisting bottle. One gram of platinum oxide powder was added to the solution. The bottle was placed on a shaking machine, evacuated from air, and pure hydrogen was passed into the bottle under 2½ atmospheric pressure till there was no more absorption. Then the catalyst was activated by removing the hydrogen, passing oxygen and shaking for five minutes, evacuating and finally passing hydrogen again. This procses was repeated till there was no more absorption of hydrogen, the time necessary for the complete reduction being four hours. Finally oxygen was passed in order to cause the precipitate to settle. Hexahydrophthalic acid, m.p. 192-193° was obtained from the filtered solution in almost theoretical yield. This was converted into its anhydride and on crystallisation first from acetic anhydride and then from absolute alcohol gave m.p. 232° corresponding to the *cis*-variety.

Benziminazole-2-hexahydro-o-benzoic Acid (VII).—Hexahydrophthalic anhydride (3 g.) was suspended in 30 c.c. of absolute alcohol and to it a solution of *o*-phenylene diamine (2 g.) in 20 c.c. of absolute alcohol was added. The mixture was refluxed for three hours on a water-bath. On cooling a precipitate came down, which was filtered off. The product was treated with a hot solution of sodium carbonate. A part of it went into solution which was filtered off from the residue (A). On acidification of the filtrate with concentrated, hydrochloric acid it gave a flocculent precipitate, which was washed with acetone and ether to remove colouring and soluble impurities. It was finally crystallised from nitrobenzene in colourless crystals, m.p. 245-247° with previous softening at about 200° (yield, 60 per cent). The compound is soluble in most solvents. (Found: N, 11·53. $C_{14}H_{16}O_2N_2$ requires N, 11·47 per cent.).

o-*Aminohexahydrophthalanil* (VI).—The residue (A) from the above experiment was crystallised from xylene when it gave colourless prismatic needles. Yield 30 per cent.; m.p. 195-196°. (Found: N, 11·52. $C_{14}H_{16}O_2N_2$ requires N, 11·47 per cent.).

Acetyl Derivative.—The anil was dissolved in glacial acetic acid and acetyl chloride was added to it drop by drop and the mixture was refluxed for about half an hour. When it was cooled a flocculent precipitate came down. It was crystallised from alcohol in colourless needles, m.p. 261-263°. (Found: N, 9·61. $C_{16}H_{18}O_3N_2$ requires N, 9·79 per cent.).

(1′ : 2′)-*Hexahydrobenzoylene*-1 : 3-*benziminazole* (VIII).—Benziminazole-2-hexahydro-o-benzoic acid (5 g.) was heated under reflux with acetic anhydride (25 c.c.) for about an hour. Then the solution was poured into water and treated with an excess of sodium carbonate. The semi-solid pasty mass was purified like compound (V) and then crystallised from alcohol in colourless prismatic needles, m.p. 175-176°. (Found: C, 74·29; H, 6·2; N, 12·35. $C_{14}H_{14}ON_2$ requires C, 74·34; H, 6·19 ; N, 12·39 per cent.).

Ethyl Benziminazole-2-hexahydro-o-benzoate.—Hexahydrobenzoylene-1 : 3-benziminazole (2 g.) was made into a paste with a small quantity of absolute alcohol. A few drops of sodium ethylate solution were added and the mixture was boiled for half an hour. The clear solution was then poured into an excess of water. The ester which was precipitated crystallised from dilute alcohol in colourless microscopic needles, m.p. 163-164°. (Found: C, 70·72; H, 7·09; N, 10·49. $C_{16}H_{20}O_2N_2$ requires C, 70·58; H, 7·35 ; N, 10·39 per cent.).

o-*Aminotolylamidohexahydrophthalic Acid*.—o-Tolylene diamine hydrochloride (5 g.) was dissolved in 30 c.c. of absolute alcohol. To this were added a suspension of hexahydrophthalic anhydride (4 g.) in 20 c.c. of absolute alcohol and fused sodium acetate (2·5 g.). The mixture was heated under reflux for four hours. On cooling it was filtered from the sodium chloride residue. The filtrate was evaporated to half its bulk, when crystals were deposited, which were separated from the mother-liquor, treated with hot sodium carbonate solution and filtered from the insoluble residue (A).

The filtrate from (A) was treated with dilute hydrochloric acid till it was acidic to congo-red paper, when a small quantity of precipitate was obtained. This was crystallised from alcohol in colourless prisms, m.p. 264-266°, which are insoluble in chloroform and ether, sparingly soluble in alcohol, but easily soluble in dilute acids, alkalis and alkaline carbonates. The yield of this acid is very low, being about 15 per cent. (Found: N, 10·01. $C_{15}H_{20}O_3N_2$ requires N, 10·15 per cent.).

o-*Aminotolylhexahydrophthalimide*.—The residue (A) described in the above experiment was crystallised from a mixture of benzene and alcohol in colourless prisms, m.p. 274-276°. They are insoluble in ether and xylene but, soluble in acetone, alcohol, pyridine, ethyl acetate, etc. (Found: N, 10·67. $C_{15}H_{18}O_2N_2$ requires N, 10·85 per cent.).

The *acetyl* derivative was crystallised from dilute alcohol; m.p. 289-291°. (Found: N, 9·23. $C_{17}H_{20}O_3N_2$ requires N, 9·33 per cent.).

(1′:2′)-*Hexahydrobenzoylene*-1:3-*ethylbenziminazole*.—*o*-Aminotolylhexahydrophthalimide was heated in a metal-bath at 280° till all the vapours had ceased to evolve and there was no more frothing. On cooling, the mass was extracted with absolute alcohol and then crystallised from it in colourless prismatic needles, m.p. 186—187°. (Found: C, 74·84; H, 6·8; N, 11·81. $C_{15}H_{16}ON_2$ requires C, 75·00; H, 6·8; N, 11·67 per cent.).

Naphthiminazole-2-*hexahydro*-o-*benzoic Acid*.—The product from hexahydrophthalic anhydride (3 g.), 1:2-naphthalene diamine (3 g.) and 50 c.c. of alcohol was purified like compound (VII). The alkaline filtrate on acidification gave a precipitate which was crystallised from nitrobenzene in colourless prismatic needles, m.p. 263-265°. They are insoluble in most solvents and also in dilute hydrochloric acid. Yield was about 70 per cent. (Found: N, 9·47. $C_{18}H_{18}O_2N_2$ requires N, 9·53 per cent.).

o-*Aminonaphthylhexahydrophthalimide*.—The residue from the above experiment was crystallised from xylene in colourless needles, m.p. 241-243°, which are soluble in dilute hydrochloric acid and nitrobenzene, while insoluble in alcohol, acetone and carbon bisulphide. Yield 25 per cent. (Found: N, 9·6. $C_{18}H_{18}O_2N_2$ requires N, 9·53 per cent.).

The *acetyl* derivative was crystallised from alcohol in colourless needles, m.p. 217-218°. (Found: N, 8·2. $C_{20}H_{20}O_3N_2$ requires N, 8·3 per cent.).

(1′:2′)-*Hexahydrobenzoylene*-1:3-*naphthiminazole*.—Naphthiminazole-2-hexahydro-o-benzoic acid was converted into the iminazole according to the method described for the compound (VIII). It crystallised from alcohol in colourless plates, m.p. 223-224°, which are sparingly soluble in alcohol, benzene, xylene, nitrobenzene, etc. (Found: C, 78·76; H, 5·84; N, 10·17. $C_{18}H_{16}ON_2$ requires C, 78·83; H, 5·80; N, 10·22 per cent.).

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Studies on Hexammine Cobaltic Sulphate. Part II.

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Like the alkali sulphates, hexammine cobaltic sulphate combines with acids to give rise to acid salts. These acid salts have been investigated by several workers and three compounds belonging to this class have so far been mentioned. Unfortunately, the authors gave no details of their preparations. They are as follows:—

(*i*) $[Co(NH_3)_6]_2(SO_4)_3,H_2SO_4$ (Jörgensen, *Z. anorg. Chem.*, 1888, **17**, 458).

(*ii*) $[Co(NH_3)_6]_2(SO_4)_3,\ 2H_2SO_4$ (Benrath and Würzberg, *Z. anorg. Chem.*, 1924, **135**, 229).

(*iii*) $2\{[Co(NH_3)_6]_2(SO_4)_3\},5H_2SO_4,10H_2O$ (Klobb, *Bull. Soc. franc. Min.*, **24**, 313).

All the three compounds form well defined crystals. The first and the third compounds were known from a long time, the identity of the second being lately established by Benrath and Würzberg (*loc. cit.*) who, at the same time, threw doubt on the existence of the last one. Contradictory statements as regards the existence of the acid salts require the matter to be re-investigated. Accordingly, the equilibrium study has been extended to the case of these acid salts, as a result of which it has been definitely established that hexammine cobaltic sulphate forms three and only three acid salts with sulphuric acid. Their mode of formation and range of stability have been determined.

The Ternary System, $[Co(NH_3)_6]_2(SO_4)_3$—H_2SO_4—*Water at* 35°.

The solubility of hexammine coblatic sulphate in sulphuric acid at different concentrations have been determined, the equilibrium being studied at 35°. Pure hexammine cobaltic sulphate was prepared by the method used in the previous investigation. The cobalt in solution was estimated by electrolytic method observing the precautions stated in Part I. The free sulphuric acid was determined

by titrating with standard alkali solution using silver nitrate as an indicator. Later on, the method of conductometric titration for estimating the free acid in these acid salts was employed.

Experimental.

A weighed quantity of the salt was placed in a 100 c.c. bottle, and about 75 c. c. of the standard acid solution added. The contents of the bottle were slightly warmed by placing in a water-bath at 60°. The bottle was vigorously shaken in a mechanical shaker, and placed in a thermostat regulated at $35 \pm 0{\cdot}1°$. During this time a solid phase or phases separated out. After the solid phase had been allowed to settle, about 10 c. c. of the clear solution was pipetted off, weighed and analysed. When the equilibrium had attained, the solid phase was separated from the liquid by filtering on a small Buchner funnel, a funnel provided with a silica bed being used for filtering solutions containing a high concentration of sulphuric acid. The solid salts obtained were often pasty due to the adhering acid solution which could not be completely removed by draining. The salt was nearly dried by pressing within the folds of a blotting paper several times and analysed.

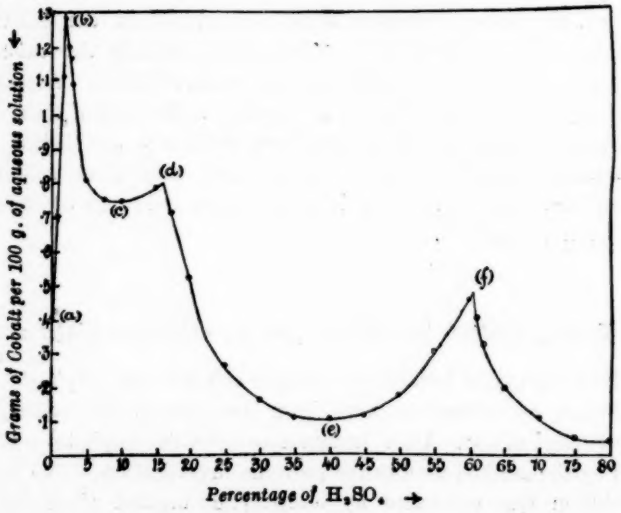

Fig. 1.

Percentage of acid.	G. of Co per 100 g. of aqueous solution.	Typical analysis of corresponding solid phases.			Remarks on solid phases.
		% Co	% SO_4 (total)	% H_2SO_4	
0	0·4013	16·82	40·68	—	Pure. $[Co(NH_3)_6]_2(SO_4)_3$.
0·75	0·7044	—	—	—	
1·5	1·1121	16·94	41·37	Minute traces.	
2	1·2806	17	41·28	,,	
2·3	1·2063	16·69	54·07	14·07	First acid salt.
3	1·0911	—	—	—	
5	0·8103	16·72	54·46	13·95	
7·5	0·7540	—	—	—	
10	0·7472	—	—	—	
15	0·7827	16·84	54·59	13·98	
17·1	0·7196	13·35	54·86	22·78	Second acid salt.
20	0·5217	—	—	—	
25	0·2590	—	—	—	
30	0·1632	—	—	—	
35	0·1141	13·57	54·29	22·35	
40	0·1125	—	—	—	
45·1	0·1182	—	—	—	
50	0·1760	13·53	54·78	22·28	
55	0·3045	—	—	—	
60	0·4629	13·55	55·15	22·68	
61	0·4037	12·41	55·65	26·23	Third acid salt.
62	0·3208	—	—	—	
65	0·1980	—	—	—	
70	0·0984	12·59	55·43	26·19	
75	0·0512	—	—	—	
80	0·0415	—	—	—	

These results have been graphically represented (Fig. 1). The abscissa represents the strength of sulphuric acid, while the ordinate

shows the number of grams of cobalt dissolved in 100 g. of aqueous solution. The solubility of the neutral salt in 0 per cent. acid (*i.e.* pure water) is represented by the point (*a*). The solubility rises with an increase in acid concentration until about 2·1% is reached, after which it gradually diminishes reaching a minimum at (*c*). The maximum (*b*), therefore, represents the first transition point. The cobalt content of the solution again increased with an increase in the acid concentration until a second maximum point (*d*) is reached. This represents a second maximum point and corresponds to about 16·1% of acid. The curve after passing through a third minimum (*e*) again rises with an increase in acid strength, until a third transition point (*f*) is reached. This point corresponds to about 60·3% of acid. After this, the curve gradually slopes down. The solubility determinations have been carried out for solutions of sulphuric acid, the strength varying from 0—80%. After this, the cobalt in solution was found to be too small for accurate analysis.

The Compounds of $[Co(NH_3)_6]_2(SO_4)_3$ *with Sulphuric Acid.*

(1) The *first acid salt* has been obtained by crystallising $[Co(NH_3)_6]_2(SO_4)_3$ from sulphuric acid solutions whose strength varies from 2·1 to 16·1 per cent. The salt crystallises in pale yellow shining crystals, which do not contain any water of crystallisation. It is freely soluble in water, the solutions being strongly acid. The salt decomposes when heated to 130°. (Found: Co, 16·56 ; total SO_4, 53·86; H_2SO_4, 13·99. $[Co(NH_3)_6]_2(SO_4)_3$, H_2SO_4 requires Co, 16·66 ; total SO_4, 54·23 ; H_2SO_4, 13·84 per cent.).

(2) The *second acid salt* has been obtained by crystallising the mother substance from dilute sulphuric acid solutions containing 16·1—60·3 per cent. sulphuric acid. It crystallises in brownish red crystals which are freely soluble in water. The air-dried product on analysis gave results which were different from those given by Benrath and Würzberg (*loc. cit.*) the results being considerably low in each case. It was, therefore, inferred that the salt contains water of crystallisation as well. In order to verify the limit of stability of the attached water molecules, the ordinary product was dried in a vacuum desiccator over sulphuric acid for a week, until it was of constant weight. By this treatment the salt neither changed in colour, nor lost its characteristic crystalline appearance. It was then analysed and the results were found to agree with those obtained

previously from the air-dried sample. Finally a weighed quantity of the air-dried product was dehydrated in a thermostat at dfferent temperatures, up to 110°. All these evidences, therefore, lead to the conclusion that the compound invariably contains water of crystallisation, which is very firmly held. The water content agrees with the formula $[Co(NH_3)_6]_2(SO_4)_3,2H_2SO_4,4H_2O$.

The salt decomposes and turns purple when heated to 125°. (Found: H_2O, 8·12 ; Co, 13·51; total SO_4, 54·8; H_2SO_4, 22·5. $[Co(NH_3)_6]_2(SO_4)_3,2H_2SO_4,4H_2O$ requires H_2O, 8·2 ; Co, 13·44 ; total SO_4, 54·7 ; H_2SO_4, 22·33 per cent.).

(3) The *third acid salt* has been obtained by crystallising $[Co(NH_3)_6]_2(SO_4)_3$ from sulphuric acid solutions whose strength exceeds 60·3 per cent. The salt forms pale yellow rhombic octahedra. It is slightly hygroscopic, and gains in weight if left for any length of time in air. On gradual heating the hydrated salt gives up its water of crystallisation until the anhydrous salt decomposes at about 125°. (Found: Co, 12·41; total SO_4, 55·4; H_2SO_4, 26·1; H_2O, 9·42. $2\{[Co(NH_3)_6]_2(SO_4)_3\},5H_2SO_4,10H_2O$ requires Co, 12·48; total SO_4, 55·88; H_2SO_4, 26; H_2O, 9·52 per cent.).

Conductometric Titration of Acid Salts with Standard Baryta Solution.

Conductivity was determined by Kohlrausch's method.
The conductivity, $C=1/R\times a/(100-a)$
where R = standard resistance and a = bridge readings.
R being constant, the quantity actually measured was $a/(100-a)$.

This is proportional to the conductivity and was plotted against the volume of reagent added.

A weighed quantity of the salt was dissolved in water so that the strengths of the acid solutions were of the order of $N/400$—$N/500$.

The standard baryta solution was added from a micro-burette graduated to 0·01 c.c. the open ends being closed by rubber tubings carrying small soda-lime tubes, for protecting the baryta from the action of carbon dioxide of the air. The conductivity of the solution was first measured. The reagent was then added and the conductivity again measured. The values were then plotted against the amount of reagent added, the composition of the salt being determined from the break in the curve.

The curves obtained are of the form shown in Figure 2. At first, the conductivity was very high, but it gradually diminished on neutralising the free acid. At a point, the conductivity was minimum, which indicates the exact neutralisation point. The

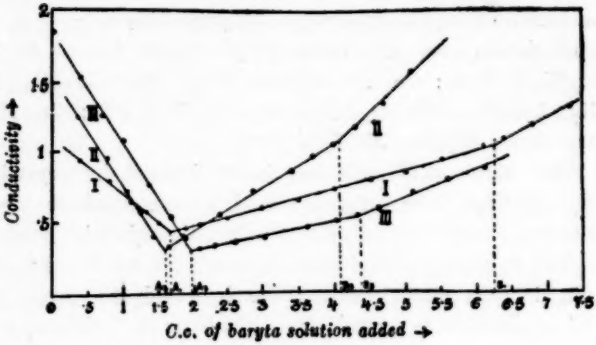

FIG. 2.

diminution of conductivity is due to the removal of hydrogen and SO_4-ions, hydrogen being most mobile of all ions. On further addition of the reagent, the conductivity again increases due to the replacement of SO_4 ions by OH-ions, the latter being most mobile next to hydrion. The second break in the curve is obtained when all the SO_4-ions are precipitated. The conductivity increases very slowly due to the increase in the concentration of both OH- and Ba-ions.

Results.

Titration of $[Co(NH_3)_6]_2(SO_4)_3,H_2SO_4$ (Fig. 2, Curve I).
Substance taken = 0·0795 g.

C.c. of baryta solution added.	Conductivity.	C.c. of baryta solution added.	Conductivity.
0	1.15	3·5	0·64
0·4	0·92	4·0	0·71
0·8	0·78	4·5	0·78
1·1	0·63	5·0	0·832
1·3	0·55	5·5	0·901
1·5	0·47	6·1	1·00
1·7	0·41	6·4	1·05
1·9	0·44	6·8	1·15
2·1	0·46	7·3	1·29
2·5	0·51	7·8	1·40
3·0	0·58		

Volume of baryta solution required to neutralise $H_2SO_4(A_1)$ = 1·66 c.c.

Volume of baryta solution required to precipitate sulphate (B_1-A_1) = 4·62 c.c.

Strength of the baryta solution = 0·14*N*.

(Found: H_2SO_4, 14·21; SO_4, 39·12. $[Co(NH_3)_6]_2(SO_4)_3$, H_2SO_4 requires H_2SO_4, 13·85; SO_4, 40·07 per cent.).

Titration of $[Co(NH_3)_6]_2(SO_4)_3,2H_2SO_4,4H_2O$ (Fig. 2, Curve II).

Substance taken = 0·0480 g.

C.c. of baryta solution added.	Conductivity.	C.c. of baryta solution added.	Conductivity.
0	1·62	2·4	0·565
0·4	1·27	2·9	0·71
0·8	0·98	3·4	0·88
1·1	0·74	3·7	0·97
1·3	0·58	4·0	1·06
1·5	0·43	4·3	1·18
1·7	0·35	4·7	1·35
1·9	0·43	5·1	1·55

Volume of baryta solution required to neutralise free H_2SO_4 (A_2) = 1·6 c.c.

Volume of baryta solution required to precipitate SO_4 (B_2-A_2) = 2·43 c.c.

Strength of baryta solution = 0·14*N*.

(Found: H_2SO_4, 22·78; SO_4, 33·9. $[Co(NH_3)_6]_2(SO_4)_3$, $2H_2SO_4$, $4H_2O$ requires H_2SO_4, 22·3; SO_4, 32·8 per cent.).

Titration of $2\{[Co(NH_3)_6]_2(SO_4)_3\},5H_2SO_4,10H_2O$ (Fig. 2, Curve III).

Substance taken = 0·0511 g.

C.c. of baryta solution added.	Conductivity.	C.c. of baryta solution added.	Conductivity.
0	1·85	2·6	0·38
0·4	1·535	3·0	0·41
0·7	1·28	3·6	0·48
1·0	1·08	4·0	0·52
1·4	0·78	4·3	0·55
1·7	0·55	4·6	0·60
1·9	0·40	5·1	0·71
2·1	0·33	5·5	0·80
2·3	0·35	6·1	0·88

Volume of baryta solution required to neutralise free $H_2SO_4(A_3)$ = 1·98 c.c.

Volume of baryta solution required to precipitate SO_4 ($B_3 - A_3$) $= 2{\cdot}35$ c.c.

Strength of the baryta solution $= 0{\cdot}14N$.

(Found: H_2SO_4, 26·4; SO_4, 30·88. $2\{[Co(NH_3)_6]_2(SO_4)_3\}$, $5H_2SO_4, 10H_2O$ requires H_2SO_4, 25·9; SO_4, 30·05 per cent.).

The results obtained show a difference from 1–3 per cent. with those obtained from theoretical calculations. These are due to–

(*a*) An increase of volume which should be avoided as far as possible, for, the conductivity measurements are related to the proportion of the ions contained in the total volume of the solution. Hence the original solution used was very dilute and the titrating reagent as strong as possible.

(*b*) The rise of temperature which, for 1°, increases the conductivity by 2 per cent. To avoid a sudden fluctuation of temperature, the beaker containing the solution was placed within a larger vessel containing water, the latter serving the purpose of a thermostat.

Summary.

From a supersaturated solution of $[Co(NH_3)_6]_2(SO_4)_3$ in sulphuric acid the following phases will crystallise out at 35°.

(1) Pure $[Co(NH_3)_6]_2(SO_4)_3, 5H_2O$ if the acid concentration be less than 2·1 per cent.

(2) If the acid concentration lies between 2·1 and 16·1 per cent. the mother substance is quantitatively transformed into the first acid salt.

(3) The second acid salt can be obtained by crystallising the mother substance from sulphuric acid solutions whose strength lies between 16·1 and 60·3 per cent. Contrary to the statements of Benrath and Würzberg (*loc. cit.*), the second acid salt is a tetrahydrated product.

(4) If the acid concentration exceeds 60·3 per cent. the third acid salt is obtained.

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Chemical Examination of the Seeds of *Caesalpinia Bonducella*, Flem. Part I.

By M. C. Tummin Katti.

The so-called bonduc seeds or " fever nuts " are obtained from *Caesalpinia Bonducella*, Flem (*Guilandia Bonducella*, Linn.), a climbing prickly shrub cosmopolitan in the tropics and common all over Bengal, Bombay and practically the whole of Southern India. These seeds have been known to Ayurvedic pharmacists for a long time as anti-periodic and the Indigenous Drugs Committee have recommended them very favourably as a powerful tonic and a valuable febrifuge.

The authors of "Pharmacographia" (Fluckiger and Hansbury, 2nd edition, p. 212) isolated a non-alkaloidal bitter principle from the kernels. Heckel and Schlagdenhauffen (*Compt. rend.*, 1886, **103**, 89) obtained from the cotyledons a non-alkaloidal bitter principle as a white amorphous powder to which they assigned the name "bonducin" and the formula $C_{14}H_{15}O_5$ and attributed to it the physiological properties of the seeds. Bacon (*Philippine J. Sci.*, 1906, **1**, Part II, 1032) was able to isolate from the kernels the bitter principle "bonducin" which he found to be not a glucoside but a mixture of complex resinous bodies. He could not obtain any alkaloid or glucoside from the alcoholic extract of the kernels. Bhaduri (*Proc. Chem. Soc.*, 1912, **28**, 53) under the title "The glucoside and the oil of *Caesalpinia Bonducella*" states that the seeds yield an alkaloid for which the author suggests the name 'natin.' No details of this brief report are published ; hence it is doubtful whether 'natin' is a glucoside or an alkaloid. Godbole, Paranjpe, and Shrikhande (*J. Indian Chem. Soc.*, 1929, **6**,

295) found that the bitter principle of the kernels extracted with alcohol contained all the sulphur of bonducella nut and reduced Fehling's solution after hydrolysis. They concluded, therefore, that the bitter principle is a glucoside.

From the preceding brief review of the literature, it will be observed that the statements respecting the physiologically active constituents of the seeds are very divergent and to a large extent, inconclusive. In view of the medicinal use of the bonduc seeds and the deficiency of our knowledge respecting their other constituents, it seemed desirable to subject them to a complete chemical examination. It was also thought possible that thereby, in conjunction with pharmacological tests, some further and more definite information might be obtained as to the character of the constituent upon which their reputed action as a febrifuge depends.

Experimental.

The material employed for this investigation consisted of a quantity of white kernels (about 40 per cent. of the whole seeds) obtained by breaking fully matured and dry seeds from the local market.

Preliminary Examination.

Test for alkaloids. 15 G. of the ground material were digested with Prollius' solution for two hours and the mixture filtered. The filtrate, on being examined in the usual manner for the presence of alkaloids, gave negative results.

Test for enzymes. 100 G. of the ground material were shaken for 18 hours with cold water. The mixture which was observed to have developed a considerable amount of gas (probably carbon dioxide) was allowed to settle. The top aqueous layer was filtered through paper with great difficulty. The filtrate was found to contain a large amount of a reducing sugar and soluble organic acids. (The original powder contained only a trace of a reducing sugar and no soluble organic acids). The presence of these compounds and the gas would indicate the existence of one or more enzymes which have probably acted upon the carbohydrate material to produce them.

Steam distillation. 300 G. of the material were distilled with steam and about 600-700 c.c. of the distillate were collected. The latter, which was not acidic, was then extracted thoroughly with redistilled ether, the ethereal liquid dried and the solvent removed. A very small amount of a pale yellow oily material (0·003 g.) was thus obtained.

Test for starch, other carbohydrates, tannin, &c. 10 G_m of the material were thoroughly mixed with 100 c.c. of distilled water and warmed on the water-bath for about half an hour. The mixture was then allowed to settle, decanted and filtered. The filtrate when tested for—

(1) starch with dilute iodine solution indicated its presence,

(2) tannin with ferric chloride indicated its absence,

(3) reducing sugar with Fehling's solution showed the presence of only a trace of some reducing sugar, and for

(4) polysaccharides (after hydrolysis with dilute hydrochloric acid) with Fehling's solution developed a heavy precipitate of cuprous oxide suggesting the presence of a considerable amount of a polysaccharide. This heavy reduction might be due to glucose formed by the hydrolysis of starch, the presence of which has already been demonstrated ; but the sweet taste of the original liquid would indicate that a disaccharide is at least partially responsible for the reduction after hydrolysis.

Extraction with different solvents. In order to ascertain the general character of the constituents, 25 g. of the ground material were extracted with various solvents successively in a Soxhlet apparatus when the following amounts of extract, dried at 100°, were obtained :

Petroleum ether (low-boiling)	extracted	4·92 g. = 19·7	per cent.
Ethyl ether	,,	0·18 g. = 0·7	,,
Chloroform	,,	0·44 g. = 1·8	,,
Ethyl acetate	,,	0·15 g. = 0·6	,,
Ethyl alcohol (95 per cent.)	,,	2·16 g. = 8·6	,,
	Total	7·85 g. = 31·4	per cent.

For the purpose of a complete examination, 15 kg. of the finely powdered material (corresponding with 37·5 kg. of the seeds) were extracted completely by percolating with cold 90 per cent. alcohol. After removal of the greater part of the solvent by distillation under reduced pressure, there remained a reddish-brown extract. This was mixed with the dry residue from another lot of 2 kg. of the powdered nut obtained after thorough extraction first with alcohol and then with petroleum ether (b.p. 60-70°) and from alcohol over the water-bath. The dry material was then extracted in a modified continuous extraction apparatus (Fig. 1) described by Sando *Ind. Eng. Chem.*, 1924, **16**, 1125), successively with low-boiling petroleum ether, ethyl ether, chloroform, ethyl acetate and lastly with ethyl alcohol and the various extracts thus obtained were examined separately.

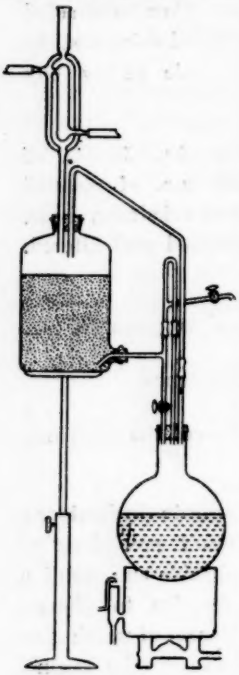

Fig. 1.

The residual powder after percolation with cold alcohol was extracted with low-boiling petroleum ether. This extract after the removal of the solvent gave a clear pale yellow, non-bitter oil (about 9 per cent. of the kernels) which has been examined separately.

I. *Petroleum Ether Extract.*

This was a viscous brown material and had a bitter taste indicating the presence of the bitter principle. In order to remove this as far as possible, the whole of the extract was shaken several times with cold 90 per cent. alcohol. The combined alcohol solution was filtered.

1. *Alcohol-soluble Portion.*

The solvent was distilled off and the residue dissolved in a very small volume of chloroform. This chloroform solution was then poured into a flask containing a large volume of low-boiling petroleum

ether. The mixture immediately turned milky and on standing in an ice-box for 5—6 days, deposited a pale yellow solid.

Isolation of the Bitter Principle (A).

The yellow solid was an amorphous powder with a very bitter taste. A larger amount of this material was subsequently obtained from the ethyl ether extract (II) and its composition and characteristics will be recorded in connection with the latter.

The mixture of the solvents from the filtrate was distilled and the brown viscous oily residue (about 125 g.) was saponified with alcoholic sodium hydroxide solution. The alcohol was then distilled and the residual strongly alkaline soap mixed with purified filter-paper pulp, dried and extracted with ethyl ether in a Soxhlet apparatus.

Examination of Unsaponifiable Matter.

The ethereal extract was washed with water and the solvent removed by distillation. As the extract was being concentrated, a white solid material began to separate out. After concentrating to a small volume and cooling, the substance was filtered and washed with ether. The filtrate on standing deposited a little more of this material which was recovered in a similar manner.

Isolation of a Phytosterolin (B) (Phytosterol glucoside).

The above mentioned white substance, m. p. 228-229°, was crystallised from ethyl alcohol in white microscopic rectangular crystals melting at 234-235°. The filtrate on concentration and cooling gave another crop of crystals melting at 232-234°. The latter is apparently an impure specimen of the same compound.

This compound gave the usual colour reactions of phytosterols. When hydrolysed with amyl alcoholic hydrochloric acid solution in the manner described by Power and Salway (*J. Chem. Soc.*, 1913, **103**, 404) in connection with the hydrolysis of ipuranol, it yielded a phytosterol (C) which crystallised from ethyl alcohol in glistening leaflets, m. p. 122-123°, and gave an acetate, m. p. 109-111°. The sugar (apparently glucose) produced by the hydrolysis was found to reduce Fehling's solution very readily but the amount was not sufficient for the preparation of the osazone.

It is therefore evident that the compound is a phytosterolin. It is interesting to note that the phytosterol (C) obtained by the hydrolysis of this compound has been isolated also in a free condition during the course of this investigation.

Isolation of a Phytosterol (D).

The ethereal filtrate after the removal of phytosterolin was distilled and the dark brown viscous residue dissolved in hot alcohol and treated with 1 per cent. hot alcoholic solution of digitonin. The phytosterol which was recovered from the precipitate in the usual manner melted at 132-133° after three crystallisations from alcohol. This compound gave the common colour reactions of phytosterols as well as an acetate melting at 119-120°. These properties indicate its identity with sitosterol.

The solvent from the alcoholic filtrate after the removal of the digitonin-phytosterol precipitate was removed by distillation and the residue freed from the excess of digitonin. The brown viscous oil (15-16 g.) thus obtained was distilled at 140-160°/ 3-4 mm. when only 3—4 g. of a light yellow oil (E) came over. All attempts to distill at higher temperatures resulted in the decomposition of the residue. The yellow oil was found to have an iodine value (Hanus) of 95·4. From the dark coloured distillation residue nothing definite could be isolated.

Examination of Fatty Acids.

These were examined in general, in the same manner as described in detail in Part II, in connection with the examination of the fatty oil. The mixture of acids was found to contain palmatic, stearic, probably lignoceric and small amounts of unsaturated acids of molecular weight lower than that of oleic acid.

2. *Alcohol-insoluble Portion.*

The dark coloured viscous oil left after the extraction with cold alcohol was saponified with alcoholic sodium hydroxide solution, the solvent distilled, and the residual soap dried on filter-paper pulp as described before. The dry soap was then extracted with ethyl ether in a continuous extraction apparatus. During the course of extraction some white solid material separated out from the extract.

Examination of Unsaponifiable Matter.

The ether extract was concentrated to about 200 c.c. and allowed to stay in the ice-box for some hours. The white solid material that had separated out was removed by filtration.

Isolation of a Phytosterolin (F),—Ipuranol, $C_{33}H_{56}O_6$.

The white solid when crystallised twice from ethyl alcohol gave a compound melting at 289-290°. This gave the usual colour reactions of phytosterols and an acetate melting at 162-163°. These results indicated its identity with ipuranol. This view was further confirmed by determining the mixed melting points of the compound and its acetyl derivative with those of ipuranol and its acetyl derivative respectively isolated from *Coscinium Fenestratum*, Cole.

Isolation of a Phytosterol (C).

The solvent from the ethereal filtrate after the removal of ipuranol was removed by distillation and the viscous oily residue which immediately solidified, was crystallised twice from ethyl alcohol. The product obtained was a snow-white crystalline substance, m.p. 122-124°. The combined filtrates on concentration gave some more of this compound. This product which yielded an acetyl derivative melting at 109-111° was identified as a phytosterol by its colour reactions. The filtrate was carefully examined ; but only a small amount of an orange-coloured oily material could be isolated from it.

Examination of Fatty Acids.

These were also examined in the same manner as described in detail in Part II. The mixture was found to contain oleic, linoleic and small amounts of unsaturated acids of lower molecular weight, together with a saturated acid of melting point 54·5°-55·5° and molecular weight 271-272. The latter was probably a mixture of palmitic and stearic acids.

II. *Ethyl Ether Extract.*

After the removal of the solvent, the extract left a dark red viscous matter which had a very bitter taste. Attempts to obtain any crystalline material from this were unsuccessful. The whole material was then dissolved in a small volume of chloroform and the

solution poured into a flask containing a large excess of low-boiling petroleum ether. The pale yellow flocculent precipitate which immediately separated out was filtered, washed with petroleum ether and dried. The mixture of solvents from the filtrate was distilled and from the small amount of the oily residue nothing definite could be isolated.

Examination of the Bitter Principle (A).

The pale yellow material when reprecipitated as described above was obtained as an amorphous almost white powder. This was mixed with the similar bitter principle obtained from the petroleum ether extract (I) and examined further.

Elementary analysis proved the absence of nitrogen, sulphur and halogens. It left no ash on ignition indicating the presence of carbon, hydrogen and probably oxygen.

It is easily soluble in alcohol, glacial acetic acid, benzene and chloroform, less soluble in ethyl ether, sparingly soluble in petroleum ether and practically insoluble in water. It dissolves in concentrated sulphuric acid with the formation of a dark brown colour. Its solution in concentrated nitric acid is yellow and in concentrated hydrochloric acid it has a pink tinge.

The melting point of the material was very indefinite. One fraction softened at 117° and completely melted at 126°. This when reprecipitated as described before gave a very pale yellow product which softened at 138° and melted at 144°. This product on a further similar treatment gave a substance which softened at 128° and melted at 133°. Thus all attempts to get a fraction of constant melting point were unsuccessful. This clearly indicated that the bitter principle was not a homogeneous compound but a complex mixture of resinous bodies.

0·5 G. of the material in neutral alcohol required 10·4 c.c. of *N*/20 sodium hydroxide solution for neutralization (phenolphthalein). The substance also dissolves in aqueous sodium hydroxide solution on warming. These reactions indicate that the bitter principle is probably an acid-resin. A chloroform solution (2 per cent.) did not show any optical activity.

The bitter powder was heated on the water-bath with 5 per cent. hydrochloric acid solution for about an hour. The mixture was filtered, the filtrate neutralised with sodium carbonate solution and treated with Fehling's solution. The mixture on being heated on

the water-bath for about 20 minutes did not develop any cuprous oxide, thus indicating the absence of any reducing sugar.

All these reactions confirm the view of Bacon (*loc. cit.*) that the bitter principle is a complex non-alkaloidal and non-glucosidic mixture of resins. The conclusion of Godbole, Paranjpe, and Shrikhande (*loc. cit.*) that the bitter principle is a glucoside containing sulphur could not therefore be verified. The reduction test they obtained after the hydrolysis of the alcoholic bitter extract is apparently due to sucrose which has been isolated from the alcoholic extract (V) and completely identified.

III. *Chloroform Extract.*

The solvent from the extract was removed and the dark red viscous residue after standing for some time had solidified. Attempts to redissolve this material in chloroform however, proved unsuccessful. Only a very small portion appeared to go in solution. The remaining material was practically insoluble in ether, acetone and alcohol; when warmed on the water-bath with chloroform the whole of the material swelled up and formed a dark red jelly. The latter when heated, lost the solvent and left a resinous product of the consistency of rubber (G). This material was not bitter but had a peculiar taste of its own. On account of its peculiar physical properties no further work could be done. From the material that was dissolved in chloroform a small amount of the bitter principle (A) was obtained.

IV. *Ethyl Acetate Extract.*

The extract after the removal of the solvent left a very small amount of a waxy residue too small for further work.

V. *Alcohol Extract.*

The residue after the removal of the solvent when dissolved in water left only a very small amount of a resinous body. The aqueous solution was treated with basic lead acetate and the yellow slimy precipitate was filtered and washed thoroughly with water.

Identification of a Saponin Material (H).

The precipitate was suspended in water, decomposed with hydrogen sulphide and the liquid filtered. The filtrate when concentrated

under reduced pressure yielded a yellow liquid which frothed considerably on shaking and yielded, on hydrolysis, a reducing sugar very readily. These properties would indicate the presence of a saponin material in the liquid.

Isolation of Sucrose (I).

After removing the excess of lead from the filtrate from the lead acetate precipitate, it was concentrated and the syrupy material that was left was digested with hot 95 per cent. alcohol. The alcohol solution was filtered and allowed to stand in the ice-box for about a week. The rhombic crystalline material that had separated out was removed and was found to soften at 161° and decompose at 168°. Its sweet aqueous solution was dextro-rotatory and reduced Fehling's solution only after hydrolysis. These properties indicated that the compound was sucrose. This view was further confirmed by the fact that its aqueous solution after being treated with the invertase preparation from yeast was laevo-rotatory and readily yielded an osazone melting at 204-205°.

Identification of Glucose (J).

The filtrate after the removal of sucrose was concentrated and the last traces of alcohol removed. The aqueous solution of the residue which reduced Fehling's solution to some extent yielded a small amount of an osazone melting at 205°. This indicated the presence of a small amount of free glucose in the aqueous solution.

Therapeutic Value of "Bonducin."

From the chemical nature of the constituents so far isolated only the bitter principle, "bonducin" seemed to have any physiological action. In order to have some idea of its activity it was administered in doses of 0·2 g. along with honey to malarious patients in one of the Ayurvedic hospitals of Poona. Six out of eight cases were reported as successful.

In connection with the isolation of the aforesaid phytosterolins and phytosterols it is interesting to note that the former as well as the latter which are obtained from the former on hydrolysis are found in the plant kingdom very frequently together. Thus the phytosterolin which yields sitosterol on hydrolysis and which was designated as ipuranol before its glucosidic nature was discovered

is commonly found in plant materials as sitosterol itself. Wherever ipuranol has been reported to occur the presence of sitosterol has also been reported; and in some cases where phytosterolins different from ipuranol are reported, phytosterols different from sitosterol are also found (*cf.* Power and Moore, *J. Chem. Soc.*, 1910, **97**, 99; *ibid.*, 1909, **95**, 1985; Rogerson, *ibid.*, 1910, **97**, 1004; Power and Salway, *ibid.*, 1913, **103**, 191.) Probably these phytosterolins would have yielded the corresponding phytosterols on hydrolysis. Such is the case with the phytosterolin melting at 234°-235°. Though a large number of phytosterols have been reported so far, the number of phytosterolins found so far are very small. This is due to the fact that the latter occur in plant materials in very small amounts and their isolation and subsequent identification therefore, is very difficult unless a large amount of the crude material is handled.

Looking over the various constituents isolated and their properties it seems evident that ' bonducin ' is the active principle of the seeds; but a correct conclusion respecting its activity could apparently only be formed when it is tested more systematically with reference to its particular value as a febrifuge.

Summary.

Preliminary examination of the kernels of *C. Bonducella* showed the presence of enzymes, starch, a small amount of a reducing sugar, considerable amount of a disaccharide and the absence of any tannin or alkaloidal material.

The alcoholic extract of the kernels on being separated into various fractions depending upon its partial solubility in the common organic solvents and further examined, has been found to contain the following compounds:

Petroleum ether extract: ' Bonducin,' the bitter resinous acid which could be isolated only in the form of an amorphous white powder of indefinite melting point; palmitic, stearic, probably lignoceric, oleic, linoleic acids and a mixture of unsaturated acids of lower molecular weight; two phytosterolins, one melting at 234°-235° and the other melting at 289°-290° (acetate, m.p. 162°-163°) and hence identical with ipuranol; two phytosterols, one melting at 122°-123° (acetate, m.p. 109°-111°) and the other melting at 132°-133° (acetate,

m.p. 119°-120°) and hence identified as sitosterol; and an unsaponifiable unsaturated oil.

Ethyl ether extract: Mainly ' bonducin ' and a small amount of an oily material.

Chloroform extract: A very small amount of ' bonducin ' and a large amount of a semi-solid material of the consistency of rubber.

Ethyl acetate extract: A small amount of a resinous matter.

Alcohol extract: A large amount of sucrose, saponin and a very small amount of glucose.

The author wishes to express his sincere thanks to Professor H. E. Waston for the kind interest he has shown throughout the course of the present investigation.

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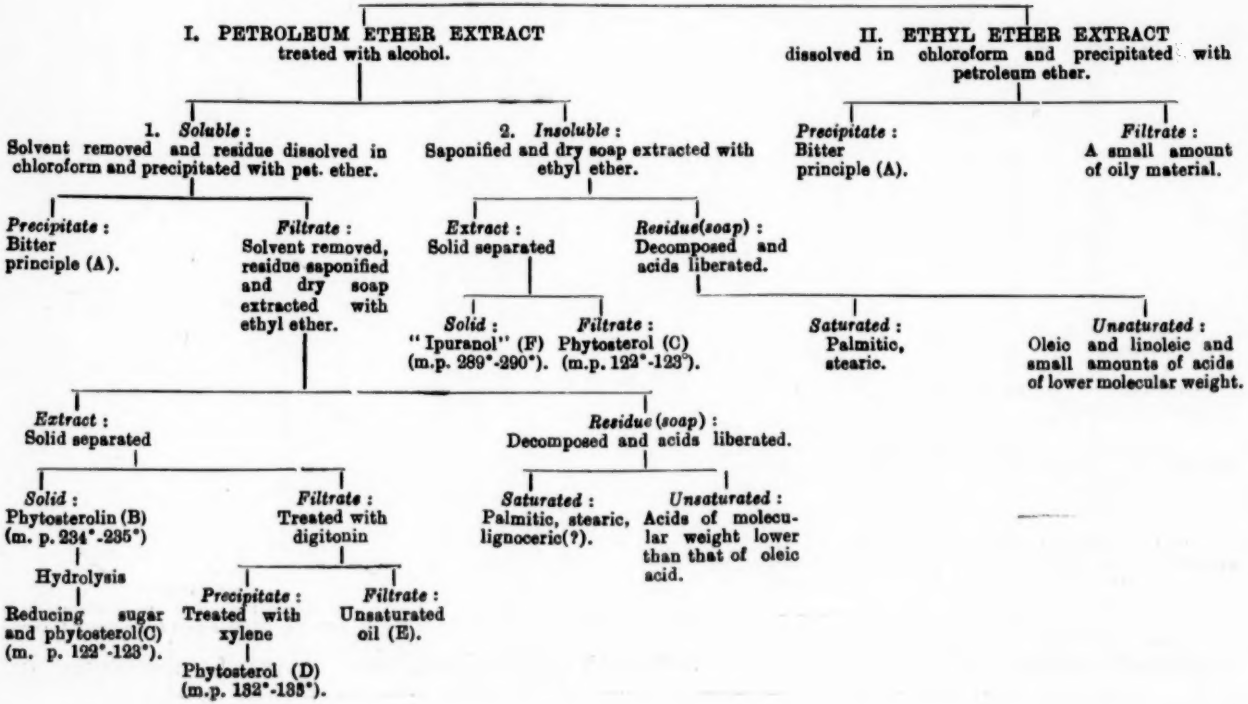
Diagramatic Scheme of Analysis of Alcoholic Extract of Kernels.


I. PETROLEUM ETHER EXTRACT
treated with alcohol.
II. ETHYL ETHER EXTRACT
dissolved in chloroform and precipitated with petroleum ether.
Precipitate : Bitter principle (A).
Filtrate : A small amount of oily material.
1. Soluble : Solvent removed and residue dissolved in chloroform and precipitated with pet. ether.
2. Insoluble : Saponified and dry soap extracted with ethyl ether.
Precipitate : Bitter principle (A).
Filtrate : Solvent removed, residue saponified and dry soap extracted with ethyl ether.
Extract : Solid separated
Residue (soap) : Decomposed and acids liberated.
Solid : "Ipuranol" (F) (m.p. 289°-290°).
Filtrate : Phytosterol (C) (m.p. 122°-123°).
Saturated : Palmitic, stearic.
Unsaturated : Oleic and linoleic and small amounts of acids of lower molecular weight.
Extract : Solid separated
Residue (soap) : Decomposed and acids liberated.
Solid : Phytosterolin (B) (m. p. 234°-235°)
Filtrate : Treated with digitonin
Saturated : Palmitic, stearic, lignoceric(?).
Unsaturated : Acids of molecular weight lower than that of oleic acid.
Hydrolysis
Reducing sugar and phytosterol(C) (m. p. 122°-123°).
Precipitate : Treated with xylene
Filtrate : Unsaturated oil (E).
Phytosterol (D) (m.p. 132°-135°).

III. CHLOROFORM EXTRACT

Bitter principle (A) and a large amount of a substance of the consistency of rubber (G).

IV. ETHYL ACETATE EXTRACT

Very small amount of a waxy residue; nothing definite.

V. ALCOHOL EXTRACT
treated with water

Soluble :
Precipitated with basic lead acetate.

Precipitate :
Treated with hydrogen sulphide and filtered.

Filtrate :

Saponin (H).

Insoluble :
Small amount of a resinous material; nothing definite.

Filtrate :
De-leaded, concentrated, digested with alcohol and crystallised.

Sucrose (I)

Filtrate :

Glucosazone (J)
(m. p. 205°).

Chemical Examination of the Seeds of *Caesalpinia Bonducella*, Flem. Part II. Fatty Oil.

By M. C. Tummin Katti and S. V. Puntambekar.

The seeds of *Caesalpinia Bonducella* being used to a considerable extent as a febrifuge, an attempt was made by one of us (M.C.T.K.) to isolate and study the nature of their active principle. In that connection the powdered kernel was extracted with cold alcohol by repeated percolation and the alcoholic extract used for further study. The residual powder when extracted with low-boiling petroleum ether yielded a pale yellow tasteless oil. Since nothing was known about the nature of this oil except some constants (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. II (6th edition), p. 246 ; Bhaduri, *Proc. Chem. Soc.*, 1912, **28**, 53) it was thought interesting to subject this to a detailed study. Very recently when the results of this investigation were being prepared for publication, a paper by Godbole, Paranjpe and Shrikhande (*J. Indian Chem. Soc.*, 1929, **6**, 295) appeared dealing with this oil. They found pamitic, stearic, oleic and linoleic acids and a crystalline sterol melting at 135°. In view of the fact that some additional compounds have been isolated from the oil we have examined, we thought it necessary to record our results here.

Experimental.

Physical and Chemical Constants of the Oil.

Specific gravity	0·9260 at 30°/30°
Refractive index	1·4745 at 28°
Saponification value	197·9
Iodine value (Hanus)	111·0
Acetyl value	35·6
Hehner value	90·9
Unsaponifiable matter	1·1 per cent.
Acid value	8·5

Chemical Constants of Mixed Fatty Acids.

Mean molecular weight	282
Iodine value (Hanus)	117·0
Saturated acids (Twitchell's method)	13 per cent.
Unsaturated acids ,, ,, ...	87 per cent.

Crude fatty acids from 500 g. of the oil were treated with a slight excess of sodium hydroxide solution. The resulting soap was dried on the water-bath with filter-paper pulp and the dry powder extracted with ethyl ether in a large Soxhlet apparatus. The ether extract was examined for unsaponifiable matter in the manner described later.

Examination of Fatty Acids.

400 G. of the total fatty acids obtained from the residual soap were separated into saturated and unsaturated acids by Twitchell's method (*Ind. Eng. Chem.*, 1921, **13**, 806). When the lead salts that were first precipitated, were dissolved in hot alcohol to be reprecipitated, a certain amount of a brown sticky material did not dissolve. This was examined separately.

Unsaturated Acids.

Methyl esters of the acids obtained only from the first filtrate were prepared in the usual manner and 47·5 g. of these esters fractionally distilled under a pressure of 6 mm. About 85 per cent. of the distillate consisted of a fraction of iodine value (Hanus) 135·3 and mean molecular weight 291 ; the remaining was distributed into four fractions of considerably lower molecular weight and iodine value. The latter, however, were too small for further work.

A portion of the major part of the esters was saponified and the alkaline soap solution oxidised with dilute potassium permanganate solution. The crude hydroxy-acids thus obtained were first extracted with petroleum ether and then with ethyl ether in a Soxhlet extractor. The petroleum ether extract was found to contain unoxidised acids and decomposition products.

The ether extract after two crystallisations from alcohol yielded an acid of melting point 129°-130° and molecular weight 316·3. These properties correspond very closely with those of dihydroxystearic acid.

The residue after the ether extraction gave after four crystallisations from alcohol an acid of melting point 158°-160° and molecular

weight 348·5. This acid is no doubt a tetrahydroxystearic acid (sativic acid). Although the melting point is lower than that usually assigned to the latter (173°) it has been noted, however, by many investigators (Power and Barrowcliff, *J. Chem. Soc.*, 1903, **87**, 899; Power and Moore, *ibid*, 1910, **97**, 1103; Power and Salway, *J. Amer. Chem. Soc.*, 1910, **32**, 350; Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. I, (6th edition, pp. 237-238) that acids agreeing in composition and character with tetrahydroxystearic acid possessed melting points varying from 156° to 165° and it is therefore possible that these compounds represent isomeric acids of the formula $C_{18}H_{36}O_6$.

It might be mentioned here that no hexahydroxystearic acid was found in the aqueous portion of the oxidation products.

When the acids from another portion of the esters were brominated according to the method of Eibner and Muggenthaler (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Vol. I (6th edition), p. 585) no hexabromides were obtained but only a pale yellow product of melting point 113°-114°, bromine content 53·4 per cent. by Stepanow method and therefore corresponding with tetrabromostearic acid was isolated.

Thus from the examination of the oxidation and bromination products, the presence of oleic and linoleic acids in the unsaturated acids has been established.

Saturated Acids.

Methyl esters of these acids were prepared in the usual manner and 36 g. of the crude esters were fractionally distilled under a pressure of 6 mm.

Fraction.	Boiling point.	Amount obtained.	Mean M.W. of acids from saponification value.
I	Below 165°	0·50 g.	265
II	165°-168°	2·60 ,,	261
III	168°-172°	13·46 ,,	268
IV	172°-174°	5·95 ,,	265
V	174°-177°	3·21 ,,	270
VI	177°-182°	3·49 ,,	274
VII	182°-185°	2·80 ,,	282
VIII	185°-195°	2·77 ,,	301
Residue and loss.	Above 195°	1·22 ,,	—
	Total	36·00 ,,	

The acids were liberated from each of these fractions and crystallised from various solvents to identify individual acids.

Fraction I. After three crystallisations from alcohol and acetone a product of m.p. 60°-62° and M.W. 263 was obtained. This seems to be impure palmitic acid.

Fraction II. The acids after four crystallisations from alcohol, acetone and ethyl acetate gave a colourless shining compound, m.p. 62°-63° and having a M.W. of 257. These properties correspond with those of palmitic acid. This view was confirmed by a mixed melting point with Kahlbaum's pure palmitic acid.

The filtrates from above yielded a mixture of acids of m.p. 55°-56° and M.W. 271-272.

Fractions III, IV, *and* V. No definite acid could be isolated in spite of the repeated crystallisations from various solvents; but a large amount of a substance of m.p. 55°-56° which remained constant after several crystallisations from various solvents and M.W. 270-272 was obtained in varying amounts.

Fraction VI. After six crystallisations from alcohol and ethyl acetate an acid of m.p. 68° and M.W. 285 was obtained. These properties very closely correspond with those of stearic acid. The identity of this acid was confirmed by a mixed melting point with Kahlbaum's recrystallised pure stearic acid.

Fraction VII. In this fraction also no definite acid was isolated; but an acid of m.p. 65° and M.W. 299 was obtained. The molecular weight indicates that this may be a mixture of stearic acid and some higher acids.

Fraction VIII. The acids after four crystallisations from alcohol and acetone yielded shining crystals of m. p. 78·5° and M. W. 369. These properties indicate that the acid is lignoceric. This view was confirmed by a mixed melting point with pure lignoceric acid kindly supplied by Mr. P. Ramaswami Ayyar.

Residue. The brown acid when crystallised three times from alcohol, acetone and ethyl acetate gave a white acid, m. p. 78°-78·5°. This was apparently lignoceric acid as its melting point did not show any change when mixed with lignoceric acid of Fraction VIII.

The acid from the brown sticky material from the lead salts of saturated acids insoluble in hot alcohol gave after several crystallisations from alcohol a product melting at 76°-77°. This seemed to be impure lignoceric acid as there was no noticeable change in its melting point when mixed with the lignoceric acid from Fraction VIII.

The m. p. 55°-56° and the M. W. 270-272 of the product from Fractions II, III, IV, and V agree very closely with those of daturic acid ($C_{17}H_{34}O_2$) as well as a mixture of palmitic and stearic acids in equimolecular proportions. In order to have some more information concerning this acid, the following additional tests were carried out with the limited amount of the material at hand.

1. About 0·5 g. of the material was dissolved in boiling alcohol and to this solution was added a boiling alcoholic solution of magnesium acetate containing just enough salt to precipitate only half the amount of the acid. The mixture on cooling deposited the magnesium salt of the acid. The melting point of the acid recovered from the precipitate was 54·5°-55·5° and that of the acid from the filtrate was 55°-56°.

2. No appreciable change was observed in the melting points of the acids from two fractions obtained by partially neutralising a certain amount of the original acid with sodium hydroxide solution and separating the acids subsequently.

3. Zinc salt of the acid was prepared in the usual manner. This had the m. p. 119°-121°. This on further crystallisation from benzene melted at 120°-121.

4. A synthetic mixture of pure palmitic acid (1·28 g.) with pure stearic acid (1·42 g.) which had the M. W. 269 and m. p. 56°-57° was crystallised from 95 per cent. alcohol. The product obtained had a M. W. of 277 and m. p. 61°-63°. This on being crystallised twice from alcohol gave pure stearic acid of m. p. 68°-69° and M. W. 283. But attempts to isolate pure palmitic acid from the first filtrate were unsuccessful even after more than six crystallisations from alcohol. The melting points and the molecular weights of compounds obtained each time varied only between 55° and 58° and 271 and 274 respectively.

Although the first three tests indicate the homogeneity of the substance, and the existence of fatty acids of odd carbon atoms in vegetable kingdom has now been fairly well established, the great difficulty of separating fatty acids by mere fractional crystallisation specially from a mixture of palmitic and stearic acids of certain composition as shown by the fourth test, renders any definite conclusion with respect to this product very doubtful.

Thus from the examination of the total saturated acids the presence of palmitic, stearic and lignoceric acids has been definitely proved. No attempts are made to calculate the percentage of each

of these acids in the oil, as we do not know definitely the nature of the intermediate fractions we have obtained. Godbole, Paranjpe, and Shrikhande (*loc. cit.*) report the presence of only palmitic and stearic acids in the saturated acids of the oil they have examined. They have definitely isolated and identified only stearic acid; the presence of palmitic acid has been assumed from the molecular weight of a mixture which might have contained this acid. The absence of lignoceric acid is, we think, due to small amounts (6·56 g.) of the total saturated acids they have handled from the original oil and to the presence of an unusually large amount of stearic acid in the acids from the hydrogenated oil, rather than to the different source of the oil they have examined.

Examination of Unsaponifiable Matter.

When the viscous residue from the ether extract of the dry soaps was dissolved in hot alcohol, an appreciable amount of an oily material separated out. This was removed by filtration and the filtrate on cooling deposited fine colourless leaflets melting at 117°-120°. This product on being recrystallised twice from alcohol gave a product, m. p. 122°-123°. This substance gave the usual colour reactions of phytosterols and an acetate of m. p. 109°-111°.

The filtrate from above was concentrated to a thick syrup which on standing for nearly a week deposited some crystals. These on subsequent crystallisation from alcohol yielded colourless plates, m. p. 132°-133°. This compound also gave the common colour reactions of phytosterols and an acetate of melting point 119°-120°. The melting points of the compound and its derivative indicate its identity with sitosterol.

The oily material which separated out from the hot alcohol solution of the ether extract, solidified on cooling. This, when crystallised thrice from a comparatively large volume of alcohol, gave colourless microscopic needles melting at 58°-59°. The insolubility of this compound in concentrated sulphuric acid even on warming on the water-bath for some time indicates that it is probably a saturated hydrocarbon. The compound was analysed with the following results. (Found: C, 85·5; H, 15·3; M. W. [by Rast's method, *Ber.*, 1922, **55**, 1051], 393. $C_{27}H_{56}$ requires C, 85·3; H, 14·7 per cent. M. W., 380).

These properties correspond very closely with those of heptacosane and this compound no doubt seems to be identical with the similar one isolated by Power and Tutin (*Arch. Pharm.*, 1907, **245**, 340) from the leaves and stems of *Lippia Scaberrima*.

Summary.

The oil from the kernels of the seeds of *Caesalpinia Bonducella* which were first extracted with alcohol to remove the bitter principle, has been found to contain the glycerides of palmitic, stearic, lignoceric, oleic and linoleic acids; two phytosterols, one melting at 122°-123° and the other identified as sitosterol, and a hydrocarbon of melting point 58°-59° which was proved to be identical with heptacosane.

In the absence of any hydroxy-acids in the oil, the high acetyl value may be accounted for by assuming the presence of some mono- or di-glycerides, which though uncommon in vegetable oils is not impossible.

We wish to express our thanks to Dr. M. O. Forster, Dr. H. E. Watson and Dr. P. C. Guha for their interest in this work.

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Photochemical Reaction Between Fatty Acids and Chlorine in Carbon Tetrachloride Solutions.

By Kali Pada Basu and Nihar Chandra Roy.

To elucidate the primary action of light on chlorine and the mechanism of photochemical reactions involving chlorine in solution, one of us (K. P. B.) has already studied the photochemical reaction between cinnamic acid and chlorine (*J. Indian Chem. Soc.*, 1929, **6**, 341) and between *cyclo*hexane and chlorine (*ibid*, 1929, **6**, 691). The present paper deals with the reaction between some aliphatic compounds (acetic, propionic and *n*-butyric acids) and chlorine.

Benrath and Hertel (*Z. wiss. Phot.*, 1924, **23**, 30) showed that these acids are chlorinated in carbon tetrachloride solutions under stimulus of radiation from a quartz mercury lamp. They performed only one experiment with each acid in white light and the initial concentration of chlorine was about double that of the acids.

We have thoroughly investigated these reactions using different concentrations of the acceptor acids and of chlorine in both white and monochromatic radiation. We have determined the quantum efficiency, temperature coefficient, and dependence on the intensity of incident radiation of these reactions. It might be mentioned at the very beginning that even so far as the kinetics of the reaction is concerned, which was the only thing studied by Benrath and Hertel, we have obtained quite different results.

We might also state that a large amount of experimental work has been done since the work of Steiner in 1874 (*Ber.*, 1874, **7**, 184) up to the present time (*cf.* Watson, *J. Chem. Soc.*, 1925, **127**, 2067) on the bromination in the dark at a high temperature (1000°) of fatty acids. The reaction appears to be very complex and the final word has not yet been said on the reaction.

On the other hand, as will appear from the present paper, the photo-chlorination of these acids is a relatively simple reaction.

The chlorine solutions in carbon tetrachloride were prepared by a method already recorded (*J. Indian Chem. Soc.*, 1929, **6**, 341). Purest samples of acetic, propionic and *n*-butyric acids of Kahlbaum were dried over phosphorus pentoxide and redistilled. The reaction

vessel was a cell ($4 \times 4 \times 1$ cm.) with plane parallel-glass sides. It was placed inside a double jacketted metal-box maintained within $\pm 0{\cdot}1°$ by circulation of water from a thermostat by means of a pump. The reaction cell had a narrow opening at the top provided with a closely fitting stopper. The reaction was followed by pipetting out 2 c.c. from time to time and the chlorine determined iodometrically with $N/200$ or $N/300$-sodium thiosulphate which was prepared afresh and standardised before each experiment.

The Dark Reaction.

In perfectly dry carbon tetrachloride solutions the reaction between chlorine and the acids is negligible at 30·5° in the dark.

TABLE I.

Acetic acid $= M/3$.	Chlorine $= M/64$.		Temp. $= 30{\cdot}5°$.	
Time in mins.	0	72	360	1200
$N/200$-Thiosulphate. ...	12·45	12·45	12·40	12·30 c.c.

The dark reactions in the cases of propionic and butyric acids are also negligible.

The reactions proceeded fairly quickly under stimulus of radiation from a quartz mercury lamp run from a storage battery at a constant current of 3 amperes. The chlorination of acetic acid proceeded most slowly and the rate increased gradually from acetic to butyric acid. The kinetics of the reaction was studied in white light and a glass cell of plane parallel sides, 4 cm. thick and containing water, was placed before the reaction cell. The use of glass-filter and glass-reaction vessel precluded the possibility of decomposition of either carbon tetrachloride or the aliphatic acids by the extreme ultra-violet radiations.

In the chlorination of acetic acid the distance between the mercury lamp and the reaction cell was 10 cm., in the case of propionic acid 14 cm., and in the case of butyric acid 12 cm. In their experiments Benrath and Hertel found an induction period and also found that the reaction followed a course given by the empirical relation $p_t - p_o = k \log t$ where p_t and p_o represent the change in chlorine concentration after time t after the lapse of induction period and just after the induction period respectively. We could not detect any appreciable induction period in any of our experiments. We also found the reaction to be perfectly unimolecular

with respect to chlorine. Benrath and Hertel do not mention how they prepared chlorine and some impurity in their chlorine might account for the observed period of induction. The peculiar course of the reaction observed by them might be explained by the fact that the chlorine concentration employed by them being nearly double that of the acceptor acids, all the excited chlorine molecules or atoms formed by absorption of radiation could not find an acceptor molecule to collide and react with. In our experiments the concentration of the chlorine was always less than that of the acceptor acids.

Propionic Acid and Chlorine.

The following table summarises the different results. The value of the unimolecular constant, it will appear, is independent of the concentration of chlorine but increases slightly with increase in concentration of the acceptor. The temperature throughout was maintained at 30·5° and the reaction cell was at a distance of 14 cm. from the mercury lamp. The unimolecular constants throughout this paper are all on the basis of logarithm to the base 10, and the time is reckoned in minutes.

TABLE II.

No.	Conc. of acid.	Conc. of chlorine.	Unimol. const.
1	*M*/3	*M*/60	0·00185
2	*M*/3	*M*/116	0·00193
3	*M*/3	*M*/156	0·00171
4	*M*/15	*M*/60	0·00168
5	*M*/15	*M*/116	0·00162
6	*M*/15	*M*/140	0·00154
7	2*M*/3	*M*/60	0·00219
8	*M*/60	*M*/60	0·00143

Butyric Acid and Chlorine.

In this case also unimolecular constants were obtained the value of which increased slightly both with increase in the concentration of the acid and of chlorine. The temperature was 30·5° throughout and the distance between the lamp and the reaction cell 19 cm. Table III summarises the different results with butyric acid.

TABLE III.

Conc. of butyric acid.	Conc. of chlorine.	Unimol. const.
M/3	*M*/60	0·00201
M/3	*M*/116	0·00190
M/3	*M*/154	0·00132
M/15	*M*/60	0·00196
M/15	*M*/116	0·00154
M/15	*M*/140	0·00111
2*M*/3	*M*/60	0·00231
M/60	*M*/60	0·00177

Acetic Acid and Chlorine.

Acetic acid is chlorinated at a much less rapid rate. The unimolecular constant appears to be independent of the initial concentration of chlorine but increases with increase in the concentration of acetic acid. The distance between the lamp and the reaction cell was 10 cm. and the temperature 30·5°. Table IV summarises different results with acetic acid.

TABLE IV.

Conc. of acetic acid.	Conc. of chlorine.	Unimol. const.
M/15	*M*/50	0·00082
M/15	*M*/96	0·00080
M/3	*M*/57	0·00114

Experiments in Monochromatic Light (436$\mu\mu$)

The same filters were employed to isolate 436$\mu\mu$ as in the case of the chlorination of *cyclo*hexane. The intensity of the incident radiation was 1·9 Hefners-at-100-cm. The intensity measurements were crrried out with a Moll thermopile and a Moll galvanometer calibrated with a Hefner lamp at a distance of 100 cm. The temperature was 30·5°.

Propionic Acid and Chlorine.

TABLE V.

	Conc. of acid.	Conc. of chlorine.	Unimol. const.
1.	*M*/3	*M*/56	0·00048
2.	2*M*/3	*M*/62	0·00062

Butyric Acid and Chlorine.

TABLE VI.

	Conc. of acid.	Conc. of chlorine.	Unimol const.
1.	$M/3$	$M/55$	0·00101
2.	$2M/3$	$M/62$	0·00109

Acetic Acid and Chlorine.

The chlorination of acetic acid under these conditions proceeded very slowly. The following table indicates the change in thiosulphate titre at different intervals.

TABLE VII.

Acetic acid $= 2M/3$. Chlorine $= M/58$.

Time in mins.	... 0	66	141	242
/200-Thiosulphate	... 13·9	13·60	13·2	12·8 c.c.
Unimol. const.	...	0·00014	0·00016	0·00014
			Mean	0·00015

Application of Einstein's Law.

The light absorbed by the reacting systems was found by taking galvanometer readings with the reaction cell filled with carbon tetrachloride and then with chlorine solution of requisite strength. 1 Mm. of galvanometer deflection corresponded to an energy of 9 ergs per sq. cm. per sec.

Acetic Acid (Table VII).—The light absorbed corresponded to 27 mm. No. of quanta absorbed per sq. cm. per sec.

$$= 27 \times 9 \times \frac{436 \times 10^{-7}}{3 \times 10^{10}} \times \frac{1}{6{\cdot}5 \times 10^{-27}} = 5{\cdot}4 \times 10^{13}.$$

The change in chlorine concentration equals 0·3 c.c. of $N/200$ in 2 c.c. in 66 minutes. No. of molecules transformed per sq. cm. per sec.

$$= \frac{0{\cdot}3}{2} \times \frac{1}{66 \times 60} \times \frac{1}{400 \times 1000} \times 6{\cdot}1 \times 10^{23} = 5{\cdot}7 \times 10^{13}.$$

For every quantum of light ($436\mu\mu$) absorbed one molecule of chlorine enters into reaction.

Propionic Acid (Table V, 2).—The light absorbed, corresponded to 24 mm. No. of quanta absorbed per sq. cm. per sec. therefore $=4{\cdot}8\times10^{13}$.

No. of mols. transformed per sq. cm. per sec.$=23{\cdot}8\times10^{13}$.
The quantum efficiency is therefore 5.

Butyric Acid (Table VI, 2).—The light absorbed corresponded to 24 mm.

No. of quanta absorbed per sq. cm. per sec.$=4{\cdot}8\times10^{13}$.
No. of mols. transformed per sq. cm. per sec.$=38{\cdot}9\times10^{13}$.
The quantum efficiency is therefore 8.

Temperature Coefficient at 436μμ.

A temperature much lower than 25·5° could not be employed as that was found to result in the deposition of moisture. The following experiments were performed at 25·5° and the intensity of incident monochromatic radiation was the same as in the previous experiments. The chlorination of acetic acid being very slow was not attempted at the lower temperature.

TABLE VIII.

Temp.$=25{\cdot}5°$.

Name of acid.	Conc. of acid.	Conc. of chlorine.	Unimol. const.
Propionic ...	*M*/3	*M*/58	0·00041
The corresponding value at 30·5° (Table V, 1) is 0·00048			
Butyric ...	*M*/3	*M*/62	0·00088
The corresponding value at 30·5° (Table VI, 1) is 0·00101			

The temperature coefficient of propionic acid, therefore, equals $\left(\frac{0{\cdot}00048}{0{\cdot}00041}\right)^2=1{\cdot}41$; and the temperature coefficient of butyric acid, therefore, equals $\left(\frac{0{\cdot}00101}{0{\cdot}00088}\right)^2=1{\cdot}32$.

Influence of the Intensity of Incident Radiation.

Butyric Acid. A lower intensity of monochromatic radiation (436μμ) was employed than in the case of Table VI, 2. The ratio

of the intensities in Table VI, 2 and Table IX was, as found by galvanometer deflections equal to $\left(\frac{188}{128}\right)=1{\cdot}47$.

Table IX gives the result at the lower intensity.

TABLE IX.

Butyric Acid. Intensity of incident radiation ($436\mu\mu$) = 1·28 Hefners-at 100 cm. Temp. = 30·5°.

Conc. of acid.	Conc. of chlorine.	Unimol,. const.
2*M*/3	*M*/54	0·00070

The ratio of the velocity constants is thus $= \frac{0{\cdot}00109}{0{\cdot}00070} = 1{\cdot}56$.

The reaction is, therefore, directly proportional to the intensity of incident radiation.

Propionic Acid. As the reaction is a slower one, a lower intensity of monochromatic light was not employed. The reaction was carried out in a lower intensity of white light than in Table II, 7. The ratio of the intensities in Table II, 7 and Table X as found by galvanometer deflections with a resistance of 200 ohms in series, was $\frac{274}{138} = 2{\cdot}0$. Table X gives the reaction at a lower intensity of white light.

TABLE X.

Propionic Acid.

Intensity of incident radiation = 1·38 Hefners. Temp. = 30·5°.

Conc. of acid.	Conc. of chlorine.	Unimol. const.
2*M*/3	*M*/69	0·00118

The mean constant at the higher intensity was 0·00219. The ratio of the constants is thus $\frac{0{\cdot}00219}{0{\cdot}00118} = 1{\cdot}86$. The reaction is thus directly proportional to the intensity of incident radiation.

Acetic Acid. The reaction is so slow that a lower intensity of white light even could not be employed. From analogy it might be expected that the relation will be the same in this case as well.

Theoretical.

The main features of these reactions are similar to those in the case of cinnamic acid and *cyclo*hexane. The temperature coefficient and the influence of the intensity of incident radiation are the same. These chlorinations are not, however, affected by the increasing concentration of hydrochloric acid which is continually generated as a result of reaction. This is remarkable since the bromination of these acids in the dark at high temperatures has been shown by various investigators (*cf.* Watson, *loc. cit.*) to be markedly accelerated by acids. This shows that the mechanism of the photochlorination is fundamentally different from the bromination in the dark.

The primary action of effective radiation ($\lambda = 4785A°$) is, as has been abundantly made clear in the previous communications, is the dissociation of chlorine molecule into an excited and a normal atom as indicated below.

$Cl_2 + h\nu \longrightarrow Cl + Cl$.....(1)

Indicating an acceptor molecule of acid by HA the following reaction then takes place.

$HA + Cl + Cl \longrightarrow ClA + HCl$.....(2)

If we assume, as has been done in previous communications that the reverse action $Cl + Cl \longrightarrow Cl_2$ is extremely slow compared to reaction (2), we can very easily explain the unimolecular nature of the constant and its direct proportionality with the intensity of incident radiation. Assuming, therefore, that the velocity of reaction is essentially governed by the rate of production of chlorine atoms, we have

$$\frac{dx}{dt} = KI_o(1 - e^{-\epsilon cd}) = KI_o\epsilon cd$$

where I_o = intensity of incident radiation,
ϵ = extinction coefficient,
c = concentration of chlorine,
d = depth of solution,

when, as was the case in our experiments, the absorption is small.

This demands that the quantum efficiency should be unity. This demand is actually fulfilled in the case of acetic acid. But in the case of propionic and butyric acids the quantum efficiency is slightly higher. This might be due to the fact that greater energy liberated in the two latter cases might initiate some sort of chain reaction.

Summary.

The kinetics of the photo-chlorination of acetic, propionic and *n*-butyric acids have been studied in white as well as in monochromatic light. In all cases unimolecular constants with respect to chlorine are obtained that vary slightly with the concentration of the acceptor.

The unimolecular constant is directly proportional to the intensity of incident radiation. The temperature coefficient in blue light (436 $\mu\mu$) is about 1·4 in all cases.

The quantum efficiency is unity in the case of acetic, 5 in the case of propionic and 8 in the case of *n*-butyric acids.

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A Study of the Interaction of Selenium Tetrachloride with Substances Containing the Reactive Methylene Group.

By K. G. Naik and R. K. Trivedi.

Interactions of 1:3-diketones with selenium tetrachloride seem to have been studied by various workers.* The subject matter of the present paper consists of a study of the interaction of selenium tetrachloride with the substituted amides of malonic acid. It was undertaken with a view to study the reactivity of the hydrogen atoms of the methylene ($-CH_2-$) group in amides and substituted amides of malonic acid.

In view of the decomposition of selenium tetrachloride studied by Taylor, Prideaux and Pool (*J. Amer. Chem. Soc.*, 1926, **48**, 2129), it is not improbable that in the present interaction it may decompose as—

$$2SeCl_4 = Se_2Cl_2 + 3Cl_2.$$

As such, it was expected that in the present interaction, the reactivity of selenium tetrachloride will be similar to that of sulphur monochloride (Naik, *J. Chem. Soc.*, 1921, **119**, 379). Selenium tetrachloride would, therefore, react with the substituted amides of malonic acid to form either chloro-compounds or selenides of the type, $>C=Se$.

It is not improbable that in the initial stage of the reaction a diselenide, $:C:Se:Se$ may have been formed, which then passes over into a monoselenide of the type $>C:Se$. This is not unusual in view of the mechanism of the reaction between ethylene and sulphur monochloride.

$$2CH_2:CH_2 + Cl_2:S:S \begin{cases} \rightarrow (CH_2Cl\cdot CH_2)_2S:S & \text{(I)} \\ \rightarrow (CH_2Cl\cdot CH_2)_2S + S & \text{(II)} \end{cases}$$

That the disulphide (I) passes into the monosulphide (II) was finally settled by the late Lieut. Col. Harrison during the great war. The second sulphur atom in this case behaves as if it were in solution (Naik, *loc. cit.*). The same may be held to be true in the case of the selenides.

* Michaelis and Kunckell, *Ber.*, 1897, **30**, 2823; Morgan and Drew, *J. Chem. Soc.*, 1920, **117**, 1456; *ibid*, 1922, **121**, 2441; Morgan and Porte, *ibid*, 1924, **125**, 1272.

In the present case it was found that selenium compounds of the type (*b*) >C : Se, were only formed. It was also interesting to find out the exact conditions under which selenides could be obtained, as also those governing the formation of the chloro-compounds.

With the above purpose in view selenium tetrachloride was made to react with the following substituted amides :—

(1) Malon-diphenylamide, (2) Malon-di-*p*-tolylamide, (3) Malonid-*m*-tolylamide, (4) Malon-di-*β*-naphthylamide, (5) Methylmalon-diphenylamide, (6) Methylmalon-di-*p*-tolylamide, (7) Methylmalon-di-*m*-tolylamide, (8) Methylmalon di-*β*-naphthylamide, (9) Malon-dibenzylamide, (10) Malon-dipropylamide, (11) Malon-diheptylamide, (12) Malon-di(1 : 3 : 4)xylidide, (13) Malon-di(1 : 4 : 5)xylidide, (14) Malon-di-α-naphthylamide, (15) Malonamide, (16) Malonmonophenylamide, (17) Malonmono-*p*-tolylamide, (18) Malon-*p*-tolylamate, (19) Malonic ester.

The main results of the present investigation can be summarised as under :—

Type I—Amides which interact to form selenides. Compounds from (1) to (8) interact to form selenides of the type, $(\text{-CO·C·CO-})_2$ with Se above the C.

Type II—Amides which interact to form chloro-compounds. Compounds from (9) to (13) react to give substances of the type, $\text{-CO·CCl}_2\text{·CO-}$

Type III—Amides which do not interact with selenium tetrachloride. Substances (14) to (17) do not react.

Compounds (18) and (19) form resinous products with selenium tetrachloride.

Type I.—The first compound of this series was prepared by the action of selenium tetrachloride on malon-diphenylamide in dry ether, at ordinary temperature (27-30°). The course of the reaction can be represented as—

$$5(\text{PhHNH·CO})_2\text{CH}_2 + 4\text{SeCl}_4 = 5(\text{PhHNH·CO})_2\text{CH}_2 + (2\text{Se}_2\text{Cl}_2 + 6\text{Cl}_2)$$
$$= 2(\text{PhNH·CO})_2\text{C : Se} + 3(\text{C}_6\text{H}_4\text{Cl·NH·CO})_2\text{CH}_2 + 10\text{HCl} + 2\text{Se}.$$
(I) (II)

That the raction actually follows the course shown above is based on the following considerations :—

(1) Of the malon-diphenylamide used, only a small quantity was utilised to form the selenide (I), as was evident from the yield.

(2) The chloro-compound (II) was obtained in a large yield, though it was very difficult to get it in a pure condition, owing to the presence of free selenium in colloidal condition.

(3) The observations of Taylor, Prideux and Pool regarding the decomposition of selenium tetrachloride (*loc. cit.*) also lend support to the view that the reaction follows the course represented by the the equation given above.

That the selenide (I) has the constitution shown above is evident from the following observations:—

(*i*) The two hydrogen atoms eliminated in the formation of the selenide (I) are not those which were originally attached to two nitrogen atoms, because on hydrolysis with aqueous potassium hydroxide, the corresponding derivative of malon-di-β-naphthylamide broke down giving β-naphthylamine.

(*ii*) The above fact also supports the view that the hydrogens eliminated are not those from the nuclei, for if that were so, β-naphthylamine could not be formed during the hydrolysis.

(*iii*) That the hydrogens are only removed from the methylene group in the present interaction is further borne out by the reaction of methylmalon-diphenylamide with selenium tetrachloride, where a selenide of the constitution, $(Ph{\cdot}NH{\cdot}CO)_2C(CH_3){\cdot}Se{\cdot}C(CH_3)(CO{\cdot}NHPh)_2$ is formed. Here the selenium tetrachloride requires two mono-substituted methylene groups to supply the two necessary hydrogens, in spite of the fact that each molecule of methylmalon-diphenylamide has two hydrogens available either from those attached to the nitrogens or from the two nuclei.

It is evident, therefore, that the formula assigned to the selenide of malon-diphenylamide is correct. On considerations which led Morgan and his co-workers to represent selenium as tetravalent, the selenide (I) of malon-diphenylamide may be represented as—

$$(PhNH{\cdot}CO)_2:C:Se:Se:C:(CO{\cdot}NHPh)_2.$$

As the selenides so obtained, are all insoluble in ordinary solvents, it was found very difficult to determine the molecular weight of any of these compounds. The stability of these selenides when treated with sodium bisulphite, which should reduce them to the corresponding substituted malonamides, goes to strengthen the view that selenium here is rather tetravalent than divalent.

Returning now to the dichloro-compound (II), one is led to believe that the two chlorine atoms are in the nuclei, for, on trying to

reduce the dichloro-compound with hydrogen iodide by Kurt Meyer's method, the dichloro-compound was obtained unchanged. This compound is, therefore, different from the dichloromalon-diphenylamide $CCl_2(CO{\cdot}NHPh)_2$ obtained by Naik and Shah (*J. Indian Chem. Soc.*, 1926, **4**, 12) by the interaction of sulphuryl chloride and malon-diphenylamide. That the two chlorine atoms of compound (II) are in the nuclei is further borne out by the fact that on hydrolysis with aqueous potash it yielded *m*-chloroaniline.†

It seems curious that in the compound (II) the halogens should prefer the nuclear hydrogens to those of the reactive methylene group. This behaviour is easily explained on the considerations of the results obtained by Silberrad and Park (*J. Chem. Soc.*, 1925, **127**, 2449), who pointed out that in the presence of chlorides of selenium as catalysts, chlorination of benzene derivatives takes place preferably in the nucleus rather than in the side-chain.

From the above it follows that the dichloro-compound (II) should be represented as $CH_2(CO{\cdot}NH{\cdot}C_6H_4Cl)_2$.

The constitution of the two main products of the present interaction having been thus established, reactions of other subatituted amides with selenium tetrachloride were tried.

Malon-di-*p*- and -*m*-tolylamides and malon-di-β-naphthylamide reacted with selenium tetrachloride giving rise to the selenides of the type $(RNH{\cdot}CO)_2C:Se:Se:C(CO{\cdot}NHR)_2$.

In order to study whether the same type of reactivity persisted throughout the corresponding derivatives of methylmalonic acid, the following four amides, namely (5) (6), (7), and (8) (*vide supra*) were subjected to the action of selenium tetrachloride, when it was found that selenides of the general structure, $>C(CH_3){\cdot}Se{\cdot}C(CH_3)<$ were formed.

It may be noted here that malonamide, malon-monophenylamide and malonmono-*p*-tolylamide were found not to react with selenium tetrachloride. Thus the reactivity which only began to manifest itself in the case of the dianilides and ditolylamides was increasing rapidly in the case of malon-*o*- and -*p*-tolylamates, and reached its

† That the product of hydrolysis is *m*-chloroaniline is substantiated on the following grounds :—

(*i*) The acetyl (m.p. 71°) and the benzoyl derivatives (m.p. 120°) of the product were found to be identical with those obtained from *m*-chloroaniline.

(*ii*) *p* : *p*-Dichlormalonanilide melts at 261° (Chattaway and Mason, *J. Chem. Soc.*, 1910, **97**, 340), whereas our dichloro-compound melts at 175°-76°.

maximum in the case of malonic ester itself, so much so, that in the last two cases resinous products were obtained. Thus, the experimental observations afford a clear evidence that the interaction of selenium tetrachloride with the amides enumerated above depends on the total negativity of the groups attached to the two remaining valencies of the methylene carbon atom. If this carry neutral groups such as $—CONH_2$ as in malonamide, no interaction occurs. Even when the neutral character of one of the $—CONH_2$ groups is disturbed by a phenyl or a tolyl group, interaction does not start. But when the neutral character of both the $—CONH_2$ groups is disturbed by converting them into —CONHPh group, the reactivity starts. In a series like,

$CH_2(CO{\cdot}NH_2)_2$	$NH_2CO{\cdot}CH_2{\cdot}CONHPh$	$CH_2(CO{\cdot}NHC_{10}H_7)_2$
(*i*)	(*ii*)	(*iii*)
$CH_2(CO{\cdot}NHPh)$	$CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}NHPh$	and $CH_2(CO_2Et)_2$
(*iv*)	(*v*)	(*vi*)

the reactivity which is absent in (*i*) and (*ii*) starts in (*vi*) and goes on increasing, lesser and lesser time being required for the completion of the reaction. Finally in the case of (*v*) and (*vi*) the reaction proceeds so vigorously that resinous products are obtained.

The interaction of selenium tetrachloride with the amides enumerated under Type II, resulted in the formation of dichloro-compounds, thus:

$$(RNHCO)_2CH_2 + SeCl_4 = (RNHCO)_2CCl_2 + 2HCl + Se.$$

In all these cases the halogens replaced the hydrogens originally attached to the methylene carbon atom, as was evident from the fact that when such compounds were treated with potassium iodide and concentrated hydrochloric acid, the halogens were easily reduced. Of the five compounds thus prepared two, namely dichloromalon-dipropylamide and dichloromalon-dibenzylamide were identical with those prepared by Naik and Shah (*loc. cit.*). The other three are new and their constitutions are established on the same considerations as in the case of the first two dichloro-compounds. Such a type of chlorinating action of selenium tetrachloride has already been reported by Morgan and Drew (*J. Chem. Soc.*, 1920, **119**, 1452).

Experimental.

General Method of Preparation.—The amide (5 mols.) was made to react with selenium tetrachloride (4 mols.) suspended in anhydrous ether. The reactions were carried out at ordinary temperature carefully excluding moisture. Hydrogen chloride was evolved during the course of the reaction. At the end of the reaction, (usually after 8 or 10 hours) the ether was slowly evaporated off and a greenish-yellow product coated with a thin film of selenium (red variety) was obtained. The dry mass was then repeatedly extracted with dry benzene, till no red film was formed on the product on drying. To ascertain that the compound was free from selenium metal, it was treated with reduced copper gauze in boiling benzene, until the shining surface of the copper gauze no longer blackened. The product was thus completely freed from selenium.

Selenomalon-diphenylamide.—Malon-diphenylamide (1·5 g.) was made to react with selenium tetrachloride (1·0 g.) in 50 c.c. of anhydrous ether. Selenomalon-diphenylamide was isolated and purified as mentioned above. The substance was insoluble in alcohol, chloroform, benzene, ether, petroleum, carbon disulphide, carbon tetrachloride, toluene, xylene, acetic acid and acetone. It was soluble in aniline and pyridine, but on evaporating the solvents, the substance was found to have been decomposed into the original malon-diphenylamide and elemental selenium (yellowish-green amorphous powder.) It darkened at 217° and melted at 222-223° to a clear red liquid. (Found: Se, 22·98. $C_{30}H_{24}N_4O_4Se_2$ requires Se, 23·86 per cent.).

Reduction of Selenomalon-diphenylamide.—On reduction with alkaline hydrosulphide (Brand, *Ber.*, 1906, **42**, 3464) selenomalon-diphenylamide was transformed into malon-diphenylamide and hydrogen selenide. The hydrogen selenide thus formed deposited selenium (red variety) on standing, the malon-diphenylamide obtained having been identified.

Bromination of Selenomalon-diphenylamide—When compound (I) was treated with bromine, selenium bromide was produced together with $CBr_2(CO{\cdot}NHPh)_2$, which was found to be identical with the compound of Backes, West and Whiteley (*J. Chem. Soc.*, 1921, **119**, 374).

Malon-dichlorodiphenylamide.—In the course of the above reaction malon-diphenylamide was partly converted into malondichloro-phenylamide. This substance was obtained in benzene solution, used in the

extraction of selenomalon-diphenylamide. On evaporating benzene malon-dichlorodiphenylamide was obtained as a crude sticky red powder. On repeated crystallisation it was obtained in the form of colourless cubic crystals from alcohol, m.p. 175-76°. (Found: Cl, 21·70. $C_{15}H_{12}N_2O_2Cl_2$ requires Cl, 21·96 per cent.).

Hydrolysis of Malon-dichlorodiphenylamide.—The dichloro-compound (2·0 g.) was mixed with an aqueous solution of caustic potash (5 g. NaOH in 10 c.c.). The whole was then refluxed for three hours. A red-brown *liquid* separated. This was extracted with ether, and after purification was identified as *m*-chloroaniline (b. p. 231°).

*Selenomalon-di-*p*-totylamide.*—Malon-di-*p*-tolylamide (1·5 g.) and selenium tetrachloride (1 g.) in 50 c.c. anhydrous ether were employed and the resulting selenomalon-di-*p*-tolylamide was obtained after purification, as an yellow powder, m. p. 218-219°. The behaviour of this substance towards solvents was similar to that of selenomalon-diphenylamide. (Found: Se, 22·09. $C_{34}H_{32}N_4O_4Se_2$ requires Se, 22·01 per cent.).

*Selenomalon-di-*m*-tolylamide.*—This was obtained in the same way as the *para*-derivative and had in similar properties, the time required for the completion of the reaction was less in this case. It melted at 210-211°, darkening previously at 205°. (Found: Se, 21·75. $C_{34}H_{32}N_4O_4Se_2$ requires Se, 22·04 per cent.).

Selenomalon-di-β-naphthylamide.—Selenium tetrachloride (1 g.), suspended in 60 c.c. of anhydrous ether was made to react with malon-di-β-naphthylamide (1·3 g.), the reaction mixture being kept overnight. Selenomalon-di-β-naphthylamide, m.p. 220°, was obtained after the usual procedure. (Found: Se, 18·26. $C_{46}H_{32}N_4O_4Se_2$ requires Se, 18·32 per cent.).

Hydrolysis of Selenomalon-di-β-naphthylamide.—One g. of the selenide was refluxed for two hours with 20 c.c. of alcoholic potash (1 g.) when a buff-coloured solution was obtained. A flocculent white mass separated on pouring the solution into a large excess of water. This was subsequently identified to be β-naphthylamine, m. p. 111°. The filtrate deposited red selenium on standing.

Selenomethylmalon-diphenylamide.— Methylmalon-diphenylamide (2 g.) and selenium tetrachloride (1·5 g.) in 60 c.c. of anhydrous ether were used. The substance resembled the corresponding malon-diphenylamide derivative in its behaviour; m. p. 222-224°. (Found: Se, 12·42. $C_{32}H_{30}N_4O_4Se$ requires Se, 12·87 per cent.).

*Selenomethylmalon-di-*p*-tolylamide.*—The amide (2·5 g.) in 25 c. c. of dry ether and selenium tetrachloride (1·0 g.) gave a

product which was purified in the usual way. It blackens at 210° and melts at 224-225°. (Found: Se, 11·76. $C_{36}H_{34}N_4O_4Se$ requires Se, 11·95 per cent.).

*Selenomethylmalon-di-*m-*tolylamide*.—This was obtained in the form of a yellow amorphous powder by the interaction of 2·5 g. of the amide with 1 g. of selenium tetrachloride. It melted at 221°. (Found: Se, 11·63. $C_{36}H_{34}N_4O_4Se$ requires Se, 11·95 per cent.).

Selenomethylmalon-di-β-naphthylamide.—The selenide was prepared in the usual way from 3 g. of the amide and 1·0 g. of selenium tetrachloride. It was a yellow powder insoluble in all organic solvents and melted at 229-230°. (Found: Se, 9·33. $C_{48}H_{42}N_4O_4Se$ requires Se, 9·71 per cent.).

Dichloromalon-diheptylamide.—Malon-diheptylamide (1·5 g.) was treated with selenium tetrachloride (1 g.) in 30 c.c. of dry ether. At the end of 10-12 hours, both the amide and the selenium tetrachloride went into solution (pink). On evaporating the solution by means of hot air, a red pasty residue was obtained. On treatment with alcohol the pink film of red selenium was precipitated and a fairly colourless solution of the dichloro-compound was obtained. After repeated crystallisations, the substance was obtained in colourless, stout, prismatic needles, m. p. 90°. It was soluble in alcohol, chloroform, carbon tetrachloride, benzene, ether, acetic acid and acetone. (Found: Cl, 19·05. $C_{17}H_{32}N_2O_2Cl_2$ requires Cl, 19·34 per cent.).

Dicholoromalon-di-(1 : 3 : 4)*xylidide*.—This substance was obtained from malon-di-(1 : 3 : 4) xylidide (1·8 g.) and selenium tetrachloride (1·0 g.) in 50 c.c. of anhydrous ether. The pure sample formed fine colourless needles melting at 136-137°. (Found: Cl, 18·09. $C_{19}H_{20}N_2O_2Cl_2$ requires Cl, 18·53 per cent.).

Dichloromalon-di (1 : 4 : 5)*xylidide*.—This was obtained in the same way as the previous xylidide. On crystallisation it was obtained as colourless, shining, short needles, m. p. 170°. (Found: Cl, 18·26. $C_{19}H_{20}N_2O_2Cl_2$ requires Cl, 18·73 per cent.).

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A New Method of Conversion of Coumarins to *o*-Coumaric Acids.

By Rajendra Nath Sen and Duhkhaharan Chakravarti.

The troublesome method of converting coumarin to *o*-coumaric acid by boiling with a very concentrated solution of sodium hydroxide or sodium ethoxide was modified by Dodge (*J. Amer. Chem. Soc.*, 1916, **38**, 450) who obtained *o*-coumaric acid from coumarin by warming its bisulphite compound with 50 per cent. potassium hydroxide solution. Recently Dey and Row (*J. Chem. Soc.*, 1924, **125**, 561) also obtained various *o*-coumaric acid derivatives from the bisulphite compounds of the corresponding coumarins by boiling with 20 per cent. caustic potash for an hour.

The present paper deals with a new method of effecting readily the same conversion of substituted coumarins, having negative substituents such as nitro-, aldehydo-, iodo-, chloro-and bromo- in the 6-position to *o*-coumaric acid derivatives by means of (*a*) mercuric oxide (yellow or red) and (*b*) mercuric acetate, by which coumarin itself also gives a good yield of *o*-coumaric acid. These substituted coumarins, as recorded by Dey and Row (*loc. cit.*), are not easily converted to *o*-coumaric acid derivatives even by boiling with concentrated solutions of sodium hydroxide or sodium ethoxide, which often bring about complicated changes. Though geometrical inversion with the help of chemical reagents (Wislicenus, *Ber.*, 1895, **28**, 1080, 2693) and with the help of chemical reactions (Skraup, *Monatsh.*, 1891, **12**, 107; Neogi and Chatterji, *J. Indian Chem. Soc.*, 1928, **5**, 279) is known, no case appears to have been previously studied in which mercury salts have been employed.

When a very dilute alkaline solution (about one per cent.) of these substituted coumarins is boiled for about an hour with a small quantity of yellow or red mercuric oxide, the sodium salts of the coumarinic acids undergo geometrical inversion quantitatively to the salt of the *o*-coumaric acids and the free acids are obtained when the solutions are acidified. In this manner, 5-nitro-, 5-aldehydo-, 5-iodo-, 3:5-dichloro- and 3:5-dibromo-*o*-coumaric acids have easily been obtained from the corresponding coumarins, the iodo- and the aldehydo-*o*-coumaric acids being prepared for the first time.

Control experiments in the absence of mercuric oxide showed that the inversion does not take place. Incidentally it has also been

noticed that oxides of any other metal such as silver, cadmium, copper, calcium, magnesium and iron cannot bring about this inversion. The action of mercuric oxide seems to be purely catalytic as it remains unchanged at the end of the operation.

It is interesting to note that coumarin itself, 4:7-dimethyl coumarin and the hydroxycoumarins (such as β-methylumbelliferone and β-methyldaphnetin) are not inverted but undergo mercuration by similar treatment with mercuric oxide (Sen and Chakravarti, *J. Indian Chem. Soc.*, 1929, **6**, 847). The influence of a negative substituent in the 6-position in these cases of geometrical inversion to *o*-coumaric acids is confirmed by the fact that 4:6-dimethylcoumarin, in which the 6-position is occupied by a positive substituent, is not converted into the *o*-coumaric acid but is easily mercurated producing a mono-mercury derivative.

Such conversion of 6-nitro-, 6:8-dichloro- and 6:8-dibromocoumarins to the corresponding *o*-coumaric acids also takes place very readily with quantitative yields by adding an aqueous solution of mercuric acetate to a caustic soda solution of the coumarins, neutralised with acetic acid in the cold, dissolving the precipitate formed in cold caustic soda and reprecipitating with hydrochloric acid. In the case of coumarin, however, a dimercury derivative of *o*-coumaric acid has been isolated (Sen and Chakravarti, *loc. cit.*), which when boiled with hydrochloric acid, gives a good yield of *o*-coumaric acid.

Many of these substituted *o*-coumaric acids, like *o*-coumaric acid itself, exhibit a fine blue fluorescence in alkaline solution which is diminished to a slight extent in the case of dichloro- and dibromo-*o*-coumaric acids while it completely vanishes in the case of iodo- and nitro-*o*-coumaric acids.

Experimental.

Inversion with Mercuric Oxide.

5-Nitro-o-coumaric Acid.—A solution of 6-nitrocoumarin (5 g.) in caustic soda (4 g. in 100 c. c. water), is diluted with water (300 c. c.) and boiled for about an hour with powdered mercuric oxide (red or yellow, 5 g.). The cold solution is filtered from the mercuric oxide and acidified with hydrochloric acid. The yellow precipitate, thus obtained, is washed with water and dissolved in ammonia. The ammoniacal solution is filtered and acidified with hydrochloric acid and the precipitate filtered, dried and crystallised from dilute alcohol in colourless needles decomposing at 245-247° and becoming yellow on

exposure to light. This is identical with the nitro-*o*-coumaric acid described by Dey and Row (*loc. cit.*). (Found: N, 6·4. $C_9H_7O_5N$ requires N, 6·7 per cent.).

5-Aldehydo-o-coumaric Acid.—A solution of 6-aldehydocoumarin (2 g.) in caustic soda (4 g. in 125 c. c. water) is diluted with water (400 c. c.) and boiled for about an hour with mercuric oxide (3 g.). The method of isolation and purification of the compound is the same as in the previous case; crystallised from dilute alcohol, it decomposes at 220°. (Found: C, 62·1; H, 4·40. $C_{10}H_8O_4$ requires C, 62·5; H; 4·16 per cent.).

The *phenylhydrazone*, prepared in the usual manner, is crystallised from dilute acetic acid; it is an yellow substance, decomposes at 237°. (Found: N, 9·8. $C_{16}H_{14}O_3N_2$ requires N, 9·93 per cent.).

The *semicarbazone*, prepared in the usual manner, is crystallised from dilute alcohol; it decomposes at 275°. (Found: N, 16·4. $C_{11}H_{11}O_4N_3$ requires N, 16·87 per cent.).

5-Iodo-o-coumaric Acid.—6-Iodocoumarin (1 g.) is dissolved in a solution of caustic soda (2 g.) in water (50 c. c.) and the solution, diluted with water (200 c. c.) is boiled for half an hour with mercuric oxide (1 g.). The method of isolation and the purification of the compound is the same as described before. It crystallised from diluted alcohol in microcrystalline powder decomposing at 187°. (Found: I, 43·43. $C_9H_7O_3I$ requires I, 43·77 per cent.).

3:5-Dichloro-o-coumaric Acid.—6:8-Dichlorocoumarin (2 g.) is dissolved in a solution of caustic soda (4 g.) in water (25 c. c.) and the alkaline solution diluted with water (400 c. c.), and boiled for half an hour with mercuric oxide (3 g.). The compound is isolated as usual. It is crystallised from dilute alcohol; it decomposes at 242°. It is identical with the dichloro-*o*-coumaric acid of Dey and Row (*loc. cit.*).

3:5-Dibromo-o-coumaric Acid.—It is obtained from 6:8-dibromo-*o*-coumarin in a manner similar to that of the dichloro-compound. It forms needles decomposing at 230° which are identical with the dibromo-*o*-coumaric acid prepared by Dey and Row (*loc. cit.*), who records the melting point as 238°.

Inversion with Mercuric Acetate.

o-Coumaric Acid.—Coumarin (5 g.) is dissolved in caustic soda solution (5 g. in 500 c. c. water) and the cold alkaline solution is carefully neutralised with dilute acetic acid from a burette using

litmus as an indicator. Mercuric acetate (15 g.), dissolved in water (100 c. c.) acidified with acetic acid, is then immediately added from a burette and the solution stirred, when a voluminous precipitate is thrown down. The solution is then left for about half an hour and filtered. The precipitate is washed with cold water, dissolved in dilute caustic potash solution and reprecipitated with acetic acid. The precipitate (diacetoxy-mercuri-*o*-coumaric acid, m.p. 215°, *J. Indian Chem. Soc.*, 1929, **6**, 852) is boiled with water (300 c. c.) containing concentrated hydrochloric acid (10 c. c.). The boiling solution is filtered hot and the filtrate on cooling gives needle-shaped crystals of *o*-coumaric acid, m.p. 207-209°. (Yield, 3·5 g.).

This *o*-coumaric acid, on treatment with concentrated sulphuric acid on the water-bath, gives coumarin (m.p. 69°).

5-Nitro-o-coumaric Acid.—A dilute caustic soda solution of 6-nitrocoumarin (5 g.) is carefully acidified with dilute acetic acid in the cold from a burette using litmus as an indicator and an aqueous solution of mercuric acetate (12 g.) is rapidly added and the solution left for half an hour and filtered. The precipitate is washed with cold water, dissolved in cold dilute caustic potash solution and reprecipitated with hydrochloric acid. The precipitate is filtered off, dried and crystallised from dilute alcohol; decomp. 247°. It is identical with the nitro-*o*-coumaric acid prepared by Dey and Row (*loc. cit.*).

3:5-Dichloro-o-coumaric Acid.—It is obtained from 6:8-dichlorocoumarin and the method of preparation and purification of the compound is the same as in the previous case ; it decomposes at 242° and is identical with the dichloro-*o*-coumaric acid of Dey and Row (*loc. cit.*).

Dibromo-o-coumaric Acid.—It is obtained from 6:8-dibromocoumarin by a similar method.

Mercuration of 4:6-Dimethylcoumarin: Formation of 8-Acetoxymercuri-4:6-dimethylcoumarin.—An alkaline solution of 4:6-dimethylcoumarin is boiled with mercuric oxide and the filtered solution acidified with acetic acid and the precipitate thoroughly washed with water and then with alcohol and dried in a vacuum desiccator. (Found: Hg, 45·30. $C_{13}H_{12}O_4$ Hg. requires Hg, 46·3 per cent.).

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A New Gravimetric Method for the Estimation of Nickel, Cobalt and Cadmium.

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It has already been shown by one of us that hydrazine gives insoluble compounds with thiocyanates of bivalent metals, such as Ni, Co, Cd, Mn and Zn having the constitution, $[M^{II}(N_2H_4)_2](SCN)_2$ (Ray and Sarkar, *J. Chem. Soc.*, 1920, **117**, 822). In the present paper, the sensitiveness of the above reactions has been studied and it has been found to furnish a most rapid and accurate general method for the quantitative estimation of cobalt, cadmium, and nickel, if present alone. A further investigation has been made with other divalent metals of the magnisium family *viz.*, Mg, Fe^{II}, Cr^{II}, V^{II}.

The compounds, $Ni(SCN)_2,2N_2H_4$, $Co(SCN)_2,2N_2H_4$, $Cd(SCN)_2,2N_2H_4$; $Zn(SCN)_2{\cdot}2N_2H_4$ are all stable compounds and have similar chemical and physical properties. These are all sparingly soluble in water, the solubility however increasing in the order Ni, Co, Cd and Zn.

The general procedure for quantitative estimation consists in precipitating cobalt, cadmium, and nickel from the solutions of their salts, when free from other metals or from one another, as $M^{II}(SCN)_2,2N_2H_4$. The precipitate is transferred to a silica or asbestos Gooch, and washed with a dilute solution of the precipitants. Finally it is washed with absolute alcohol and dried in a steam-oven. The precipitate is weighed as $M^{II}(SCN)_2,2N_2H_4$.

Estimation of Cobalt.

When a dilute neutral solution of cobalt salt is treated with ammonium thiocyanate and hydrazine hydrate, a flesh coloured silky crystalline precipitate of cobalt thiocyanate-hydrazine is formed.

$$CoSO_4 + 2NH_4{\cdot}SCN + 2N_2H_4{\cdot}H_2O = Co(SCN)_2,2N_2H_4 + (NH_4)_2SO_4 + 2H_2O$$

The precipitate is very slightly soluble in water but insoluble in alcohol and other common organic solvents.

Limit of Sensitiveness.—The reaction is sensitive enough to detect the presence of 10^{-5} g. of cobalt per c.c. After a systematic investigation, the following procedure for the complete precipitation of cobalt was established.

Procedure.—Dilute the neutral or slightly acid solution of the sulphate, chloride or nitrate, so that not more than 0·15 g. of cobalt is present in 200 c.c.; treat with 10 to 15 times the theoretical amount of ammonium thiocyanate, heat to about 70°, stirring well. Add drop by drop, a very dilute aqueous solution of hydrazine hydrate adding two to three drops in excess and allow to settle. The precipitate is filtered through an asbetos or silica Gooch.

First Washing.—As the componnd, $Co(SCN)_2,2N_2H_4$ is slightly soluble in water but quite insoluble in alcohol, it has to be washed free from sulphate, nitrate or chloride with the following wash-liquor.

Wash-liquor.—15 C.c. rectified spirit, 75 c.c. water, 1·5 g. ammonium thiocyanate, and 0·025 g. hydrazine hydrate.

Second Washing.—The precipitate is then washed with absolute alcohol and freed from thiocyanate, hydrazine and traces of water. The alcohol is removed as far as possible by sucking a current of air through it; finally it is dried, in the steam-oven and weighed as $Co(SCN)_2,2N_2H_4$ (Co=24·7%).

When the solution contains more than 0·15 g. of cobalt per 200 c.c. oxidation takes place (in presence of an excess of ammonium sulphate, nitrate or chloride) in alkaline solution, hence the precipitation of cobalt is not complete. If, however, the precipitation be carried out in an atmosphere of hydrogen with a further increment of usual volume, quite satisfactory results are obtained. A few precautions for the successful operation of the method are as follows:

(1) The solution containing cobalt must not be highly acidic, as it involves an unnecessary expenditure of hydrazine hydrate, at the same time the precipitate assumes a brownish tint probably due to the formation of cobaltic oxide.

(2) Hydrazine hydrate must not be added in more than five times the theoretical quantity. Otherwise hydrogen sulphide which is formed to some extent causes the formation of cobalt sulphide.

(3) The filtration should be done at 35°. When filtered hot, the result is a little low.

(4) During filtration a strong current of air should not be sucked in through the precipitate until it is finally washed with

alcohol. If exposed to air for a long time in presence of the precipitants, black cobalt sulphide is sometimes formed.

(5) The precipitate when placed in the oven for drying should be free from all traces of water. Hot water decomposes the compound into a bluish hydroxide.

A few of the preliminary data which led to the establishment of the conditions are as follows:—

(*a*) *Influence of temperature.*

Temperature.	Time required to settle.	Cobalt actually present.	Cobalt found.	Error.
Precipitation carried at room temperature.	About one hour.	0·1235g.	0·1233g.	−·0002
Pptn. carried at room temp. 30°, cooled to 0° and filtered.	The ppt. settled as the temp. began to fall.	0·1235	0·1232	−·0003
Pptn. carried at a temp. above 70° and digested on the water-bath (98-99°) for 25 minutes, cooled to 30°, filtered.	Precipitate settled in 20 mins. in comparatively big grains.	0·1235	0·1230	−·0005
Pptn. carried at about 65° and cooled to 35°.	During the cooling the ppt. settled very well in less than half an hour.	0·1235	0·1234	−·0001
Pptn. carried in warm soln. at about 65° and allowed to cool and settle overnight.		0·1235	0·1232	−·0003

(*b*) *Influence of increasing concentration of ammonium thiocyanate.*

Ammon. thiocyanate used.	Cobalt actually present.	Cobalt found.	Error.
4 times the theoretical amount.	0·1235 g.	0·1234 g. (The ppt. was not so well crystalline).	−0·0001
10 times the ,,	0·1235	0·1233	−0·0002
15 times the ,,	0·1235	0·1234	−0·0001

(*c*) *Influence of excess of hydrazine.*

Hydrazine hydrate used.	Cobalt actually present.	Cobalt found.	Error.
10 times the theoretical amount.	0·1235 g.	0·1226 g.	−0·0009

A solution of extra pure cobalt nitrate free from nickel, iron and other heavy metals, sulphates, chlorides, etc., was used. The actual quantity of cobalt present, was determined by duplicate electrolytic estimations and in some cases by the sulphate method. Calibrated burettes and weights were used.

TABLE I.

Actual amount of cobalt present.	Amount of cobalt found.	Error.
0·1235 g.	0·1232 g.	−·0003
0·1235	0·1233	−·0002
0·1235	0·1232	−·0003
0·1235	0·1234	−·0001
0·1074	0·1074	−·0000
0·1074	0·1074	,,
0·0822	0·0819	−·0003
0·0658	0·0656	−·0002
0·0411	0·0410	−·0001
0·0165	0·0166	+·0001

With quantities of cobalt greater than 0·15 g. the results obtained were low but the difficulty was overcome as would be evident from the following table:—

TABLE II.

(*a*) *With quantities more than* 0·15 g. *per* 200 c.c.

Amount of cobalt present.	Cobalt found.	Error.
0·1811 g.	0·1794 g.	−·0017
0·2881	0·2853	−·0028

(*b*) *The volume was increased to* 800 c.c.

0·2881 g.	0·2865 g.	−·0016

(*c*) *In an atmosphere of hydrogen, volume as in* (*a*).

0·3222 g.	0·3210 g.	−·0012
0·2148	0·2141	−·0007

(*d*) *In an atmosphere of hydrogen and with increased volume.*

0·2148 g.	0·2146 g.	−·0002

Presence of the salts of alkalis and alkaline earth metals or magnesium does not interfere with the estimation, if the precipitations be made in an atmosphere of hydrogen with dilute solutions.

Estimation of Cadmium.

A white crystalline compound, $Cd(SCN)_2,2N_2H_4$ is obtained on adding ammonium thiocyanate and hydrazine hydrate to a cadmium solution.

Limit of Sensitiveness.—The reaction is sensitive enough to detect the presence of $1{\cdot}3\times10^{-5}$ g. of cadmium per c.c.

The compound is more soluble in water than that of cobalt. The cadmium compound is slightly dissolved even in presence of the precipitating reagents. The precipitation of cadmium is only complete either at a very low temperature or in an alcoholic medium of definite concentration at ordinary temperature. The cadmium compound is insoluble in other common organic solvents. After a systematic study, the following procedure has been adopted for a quantitative estimation.

Procedure.—Dilute the neutral or slightly acid solution, so that not more than 0·1 g. of cadmium is present in 100 c.c.; treat with 10 to 15 times the theoretical quantity of ammonium thiocyanate. Stir and carefully add drop by drop very dilute aqueous hydrazine hydrate until the precipitation begins, add two or three drops more and allow it to settle for a minute or two. Then add 50 c.c. of 30 per cent. alcohol and cool the solution below 12°. By this time the precipitate has completely settled. A silica or asbestos Gooch is used for filtration and the precipitate is washed with the following liquor:—

100 C.c. of 25 per cent. alcohol solution + 1·5 g. of NH_4SCN + 0·025 g. of hydrazine hydrate. It is finally washed with absolute alcohol and dried at a temperature below 80°. For successful operations similar precautions should be taken as in the case of cobalt.

A few of the preliminary data which led to the correct procedure are as follows:

TABLE II.

Conditions.	Cadmium actually present.	Cadmium found.	Error.
At the room temp. in aqueous soln. washed with the liquor as in the case of cobalt (aqueous).	0·1039 g.	0·1050 g.	−0·0039
After pptn. the soln. cooled below 5° and washed with alcoholic liquor.	0·1089	0·1080	−0·0009
Pptn. carried in 15% alcoholic soln.	0·1089	0·1081	−0·0008
Pptn. carried in 20 per cent. alcoholic soln.	0·1089	0·1090	+0·0001

An " extra pure " variety of Merck's cadmium sulphate guaranteed to be free from zinc, iron, etc., was used. The cadmium in solution was etimated in duplicate by the pyrophosphate method. The following estimations were made by the new method :—

TABLE IV.

Amount of cadmium actually present.	Amount of cadmium found by the new method.	Error.
0·2723 g.	0·2723 g.	0
0·2178	0·2182	+0·0004
0·1743	0·1747	,,
0·1089	0·1092	+0·0003
,,	0·1091	+0·0002
,,	0·1090	+0·0001
0·1038	0·1035	−0·0003
0·0762	0·0761	−0·0001
0·0544	0·0542	−0·0002
0·0272	0·0271	−0·0001
0·0109	0·0110	+0·0001

Estimation of Nickel.

The bluish-violet, very finely divided precipitate of $Ni(SCN)_2$, $2N_2H_4$ is practically insoluble in water and is the most stable compound of the series.

Limit of Sensitiveness.—$0·8 \times 10^{-5}$G. of nickel per c. c. can be detected.

The precipitate being very fine care must be taken during filtration and washing. Nickel is quantitatively precipitated, with any concentration of ammonium thiocyanate and hydrazine but the precipitate takes time to settle. The following procedure has been found to be the best :—

Procedure.—Dilute the neutral or slightly acid solution of nickel chloride so that 0·1 g. of Ni is present in 150 c. c. of solution ; add 2 g. of NH_4·SCN, heat to boiling, stir well and precipitate with 5 to 10 times the theoretical quantity of hydrazine hydrate. Allow the precipitate to settle for half an hour, when it is ready for filtration (the precipitate being slimy does not settle well). Filtration becomes

more easy if the precipitate be allowed to stand overnight. An asbestos or silica Gooch No. 4 is used. The precipitate is washed with the same wash-liquor as used in the case of cobalt ; finally washed with absolute alcohol and dried in a steam-oven. Weighed as the original compound $Ni(SCN)_2,2N_2H_4$. An " extra pure " sample of nickel chloride guaranteed to be free from cobalt, iron and other heavy metals was used. The actual quantity of nickel was found by duplicate estimation as nickel dimethyl glyoxime.

Amount of nickel actually present.	Amount of nickel found out by the new mtehod.	Error.
0·2255 g.	0·2255 g.	*Nil*
0·1804	0·1804	"
0·1353	0·1352	−·0001
0·0902	0·0907	−·0005
0·0451	0·0451	*Nil*
0·0390	0·0386	−·0004
0·0390	0·0390	*Nil*

Some more new compounds of the series $R''(SCN)_2,2N_2H_4$ have been prepared.

Compound of Ferrous Thiocyanate and Hydrazine.

A solution of ferrous sulphate was mixed with a concentrated solution of ammonium thiocyanate and hydrazine hydrate added drop by drop. A white crystalline precipitate was obtained which gradually turned yellowish-red on exposure to air. When the compound is formed in alcoholic solution and washed with alcohol, the compound is fairly stable. When dissolved in water a green precipitate of ferrous hydroxide is obtained. Diltue ammonia gives green $Fe(OH)_2$. The dry substance decomposes to black oxide of iron (FeO) at about 90°. (Found : Fe, 23·9 ; S, 26·8 ; N_2H_4, 27·61. $Fe(SCN)_2,2N_2H_4$ requires Fe, 23·7 ; S, 27·1 ; N_2H_4, 27·12 per cent.).

Compound of Magnesium Thiocyanate with Hydrazine.

Magnesium in addition to its relationship to calcium and other two alkaline earths shows several points of resemblance to nickel, cobalt, zinc, iron (bivalent), etc., in forming a few analogous bivalent salts, *e.g.*, isomorphous sulphates like $MgSO_4,7H_2O$; $NiSO_4$,

$7H_2O$; $CoSO_4,7H_2O$; $ZnSO_4,7H_2O$; $FeSO_4,7H_2O$; etc., and isomorphous double sulphate like $K_2Mg(SO_4)_2,6H_2O$; $K_2Ni(SO_4)_2,6H_2O$; $K_2Co(SO_4)_2,6H_2O$; $K_2Zn(SO_4)_2,6H_2O$; $K_2Fe(SO_4)_2,6H_2O$ etc., and insoluble double phosphates like $Mg(NH_4)PO_4,xH_2O$; $Zn(NH_4)PO_4,xH_2O$; $Mn(NH_4)PO_4,xH_2O$.

The bivalent oxides of magnesium and iron are constantly associated together in nature as isomorphous mixture of silicates in minerals such as olivine $(MgFe)_2SiO_4$ and hornblende $(MgFe)SiO_3$. The behaviour of magnesium suggested that a compound analogous to $R''(SCN)_2,2N_2H_2$ etc., might be obtained, by the action of hydrazine hydrate on magnesium thiocyanate. Magnesium acetate and ammonium thiocyanate were dissolved in absolute alcohol, warmed a little, an absolute alcoholic solution of hydrazine hydrate was added, and after vigorous stirring a precipitate appeared. Drained and washed with absolute alcohol, and dried, a white crystalline substance was obtained. Contrary to the previous hydrazine thiocyanate compound, it is highly soluble in water. In the dry state it is fairly stable; when heated above 60° decomposes into the oxide. (Found: Mg, 10·9 ; S, 30·08 ; N_2H_4, 30·4. $Mg(SCN)_2,2N_2H_4$ requires Mg, 11·26 ; S, 30·05 ; N_2H_4, 30·05 per cent.).

All the salts of the series $R''(SCN)_2,2N_2H_4$ described appear under the polarisation microscope double refracting and exhibit oblique extinction. Their suitability for microchemical detection specially that of zinc will be communicated shortly.

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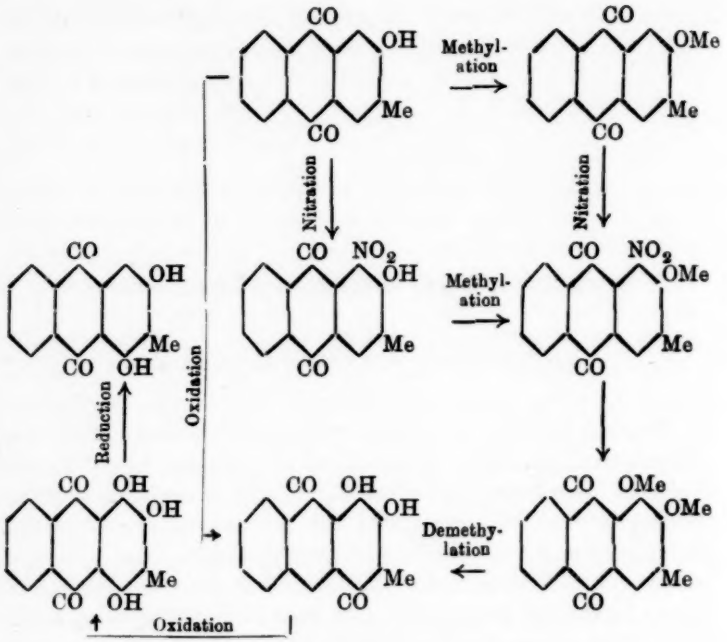
Nitration of 2-Oxy-3-methylanthraquinone.

By P. C. Mitter and Sudhir Chandra Pal.

By the nitration of 1-oxy-3-methylanthraquinone, Eder and Manoukian (*Helv. Chim. Acta*, 1926, **9**, 54) obtained 1-oxy-3-methyl-4-nitro-, 1-oxy-3-methyl-2′-nitro- and 1-oxy-3-methyl-2 : 4-dinitro-anthraquinone. We investigated the nitration of 2-oxy-3-methyl-anthraquinone in the hope of obtaining, among others, 2-oxy-3-methyl-4-nitroanthraquinone, which could be used as a convenient starting point for the synthesis of rubiadin-1-methyl ether, a substance which is present in *Morinda longiflora* (Barrowcliff and Tutin, *J. Chem. Soc.*, 1907, **91**, 1909), but which has not been hitherto synthesised.

The nitration of 2-oxy-3-methylanthraquinone under the conditions employed by Eder and Manoukian (*loc. cit.*) gave however only a mononitro-derivative, which on methylation gave a product identical with the nitration prduct of 2-methoxy-3-methylanthraquinone. The nitro-compounds can be reduced by aqueous sodium sulphide solution to the corresponding amino-compounds. On treating with potassium methoxide, the nitro-methoxymethylanthraquinone gives a dimethoxy-methylanthraquinone, which gives 3-methylalizarin on de-methylation, indicating thereby that the nitro-group had entered the position 1. On oxidation with manganese dioxide and sulphuric acid, 3-methylalizarin gives 3-methylpurpurin (Mitter and Sen, *J. Indian Chem. Soc.*, 1928, **5**, 638) which on reduction with stannous chloride in alkaline solution gives rubiadin.

Nitration of 3-methylalizarin-dimethyl ether gives a mononitro-derivative, probably the 4-nitro-compound. Attempts at replacement of the nitro-group by methoxyl have not been so far successful.



Experimental.

1-*Nitro*-2-*hydroxy*-3-*methylanthraquinone*.

Two g. of 2-hydroxy-3-methylanthraquinone (Mitter and Sen, *loc. cit.*, p. 636) were dissolved in pure concentrated sulphuric acid (5 c. c.) and finely powdered potassium nitrate (2 g.) was added in small quantities. The mixture was warmed on the water-bath for five hours and left overnight. It was then poured into water, filtered, washed with hot water, and crystallised from a large volume of glacial acetic acid in prisms, m. p. 267° (yield, 1·5 g.). (Found: N, 4·97. $C_{15}H_9O_5N$ requires N, 4·94 per cent.).

1-*Nitro*-2-*methoxy*-3-*methylanthraquinone*.

2-Methoxy-3-methylanthraquinone (2 g.) was nitrated as in the previous case, and the product crystallised from acetic acid in plates, m. p. 206° (yield 1·5 g.). (Found: N, 4·92. $C_{16}H_{11}O_5N$ requires N, 4·71 per cent.). The same substance is also obtained by the direct methylation of 1-nitro-2-hydroxy-3-methylanthraquinone.

1-Amino-2-hydroxy-3-methylanthraquinone.

1-Nitro-2-hydroxy-3-methylanthraquinone (2 g.) was dissolved in 100 c. c. of 5 % sodium sulphide solution and boiled for one hour under reflux. The deep violet solution was filtered on cooling, and the filtrate acidified with dilute hydrochloric acid, when a red precipitate came down. It was washed with water and crystallised from glacial acetic acid in needles, m. p. 215°-216° (yield, 1 g.) (Found: N, 5·04. $C_{15}H_{11}O_3N$ requires N, 5·53 per cent.).

1-Amino-2-methoxy-3-methylanthraquinone.

1-Nitro-2-methoxy-3-methylanthraquinone (2 g.) was reduced with 5 % sodium sulphide as in the previous case, the yellow nitro-compound being converted into red mass during the operation. It was filtered, washed with hot water and crystallised from rectified spirit in needles, m.p. 195° (yield, 1 g.). (Found: N, 5·49. $C_{16}H_{13}O_3N$ requires N, 5·26 per cent.).

1:2-Dimethoxy-3-methylanthraquinone.

1-Nitro-2-methoxy-3-methylanthraquinone (4 g.) was suspended in 60 c. c. of absolute methyl alcohol and 80 c. c. of potassium methylate solution (5%) added. The mixture was refluxed on the water-bath for twelve hours. On pouring into water, a brown precipitate was obtained which was filtered, washed and crystallised from dilute acetic acid in prisms, m. p. 127° (yield, 2·5 g.). (Found: C, 71·96; H, 5·04. $C_{17}H_{14}O_4$ requires C, 72·3 ; H, 4·97 per cent.).

3-Methylalizarin.—1:2-Dimethoxy-6-methylanthraquinone (2 g.) was mixed with finely powdered aluminium chloride (2 g.) and heated to 200° in course of one hour, and kept at that temperature for half an hour. When cooled, the reaction mixture was treated with water, boiled with a few c. c. of hydrochloric acid, filtered and the residue dissolved in one per cent. solution of potassium hydroxide. It was filtered and the filtrate acidified with hydrochloric acid when yellow flakes appeared. Crystallised from benzene, it was obtained in the form of needles, m. p. 245°.

Diacetyl Derivative of 3-Methylalizarin.

It was prepared in the usual way with acetic anhydride and a drop of pyridine, crystallised from alcohol in needles, m. p. 162°.

The melting point of this compound, given by Mitter and Sen(*loc. cit.*, p. 631) as 262°, is evidently due to manuscript error. (Found: C, 67·84 ; H, 3·94. $C_{19}H_{14}O_6$ requires C, 67·46; H, 4·14 per cent.).

3-*Methylpurpurin.*

Crystallised 3-methylalizarin (2 g.) was oxidized according to the method of Mitter and Sen (*loc. cit.*) and crystallised from benzene in needles, m. p. 231° (yield, 1 g.).

Triacetyl Derivative of 3-*Methylpurpurin.*

The acetyl derivative was prepared in the usual way and crystallised in needles from alcohol, m.p. 213°. (Found: C, 63·74; H, 4·2. $C_{21}H_{16}O_8$ requires C, 63·63 ; H, 4·04 per cent.).

Rubiadin.—3-Methylpurpurin (1 g.) was dissolved in ten per cent. caustic soda solution, heated to boiling and stannous chloride was added little by little until the original red colour of the solution changed to yellow, care being taken that the stannous salt remains in solution. After cooling, it was precipitated with hydrochloric acid, filtered and the precipitate digested with hydrochloric acid, filtered, washed and dissolved in baryta water, the filtrate from this solution is treated with hydrochloric acid when a yellow mass is obtained, which is crystallised from benzene. The substance has all the properties of rubiadin. It melts at 290°, and its acetyl derivative melts at 225°.

1:2-*Dimethoxy*-3-*methyl*-4 (?)-*nitroanthraquinone.*

1:2-Dimethoxy-3-methylanthraquinone (2 g.) was nitrated with potassium nitrate and sulphuric acid in the usual way and the product recrystallised from acetic acid, in needles, m. p. 248° (yield, 1 g.). (Found: N, 4·59. $C_{17}H_{13}O_6N$ requires N, 4·3 per cent.).

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Extension of Michael's Reaction. Part I.—Action of Urethane on Esters of Unsaturated Acids. Part II.—Action of Urethane on Carbimides and Thiocarbimides.

By Tejendra Nath Ghosh and Praphulla Chandra Guha.

Part I.

Condensations between sodium derivatives of acetoacetic ester and malonic ester have been studied extensively by a large number of workers (Michael, *J. pr. Chem.*,1887, **35**, 351; 1891, **43**, 395; 1892, **45**, 55; 1894, **49**, 20; Auwers, *Ber.*, 1891, **24**, 317, 2887; 1893, **26**, 364; 1895, **28**, 263, 1131; *Annalen*, 1896, **292**, 147 ; Vorländer, *Ber.*, 1894, **27**, 2053 ; *Annalen*, 1897, **294**, 253 ; Ruhemann, *J. Chem. Soc.*, 1893, **73**, 727, 1006 ; Hope, *J. Chem. Soc.*, 1912, **101**, 892 ; Ingold, Shoppee and Thorpe, *J. Chem. Soc.*, 1926, **129**, 1477 ; Ingold and Shoppee, *J. Chem. Soc.*, 1926, **129**, 1912).

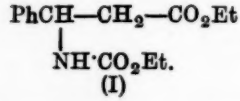
The condensation of urethane which, it is well known, readily forms sodium derivative does not appear to have been studied on the line of Michael's condensation. The only work on record appears to be that of Diels and Heintzel (*Ber.*, 1905, **38**, 297) who got ethyl cinnamoylcarbamate $Ph{\cdot}CH{=}CH{\cdot}CO{\cdot}NH{\cdot}CO_2Et$ by the direct action of ethyl carbamate on cinnamic ester. The present investigation was undertaken with two objects in view, firstly, to see whether sodium derivative of urethane lends itself like the sodium derivatives of acetoacetic and malonic esters to ordinary Michael's condensation and secondly to utilise the addition compounds, if so formed, for the preparation of amino-acids, thus—

$$R{\cdot}CH{=}CH{\cdot}CO_2Et + NaNH{\cdot}CO_2Et \longrightarrow RCH(Na)\text{—}CH(NH{\cdot}CO_2Et)\text{—}CO_2Et$$

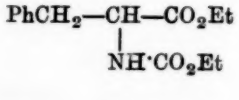
$$RCH(Na)\text{—}CH(NH{\cdot}CO_2Et)\text{—}CO_2Et \xrightarrow{\text{Hydrolysis and elimination of } CO_2} R{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$$

$$RCH(Na)\text{—}CH(NH{\cdot}CO_2Et)\text{—}CO_2Et \xrightarrow{\text{Hydrolysis etc.}} RCH(NH_2){\cdot}CH_2{\cdot}CO_2H$$

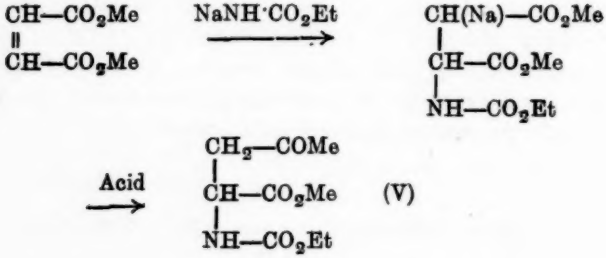
The existing methods for the preparation of amino-acids by the direct addition of ammonia and hydroxylamine to unsaturated acids are very tedious (*cf.* Curtius, *J. pr. Chem.*, 1904, **70**, 204; Engel, *Compt. rend.*, 1887, **104**, 1805). Sodium ethylcarbamate in ethereal suspension has now been found to react with ethyl cinnamate to give an addition compound which, on treatment with acid, yields a substance possessing the empirical formula, $C_{14}H_{19}O_4N$ which may possess either of the following two structures.



(I)



It was expected that the urethanylphenylpropionic ester so formed, on hydrolysis, would give aminophenylpropionic acid as urethane gives ammonia, carbon dioxide and alcohol. But on hydrolysis (*vide* Experimental) it gets decomposed into urethane and cinnamic acid and this suggests that the urethenyl group was attached to the β-carbon atom of the phenylpropionic ester. Decomposition of β-amino- and β-hydroxy-acids into ammonia or water and unsaturated acids is well known. Similar condensations have also been tried with *o*-, *m*- and *p*-nitrocinnamic esters and in each case the corresponding β-urethanyl compounds (II, III and IV) have been obtained. With the hope of getting the carbethoxy derivative of aspartic ester the action of urethane in presence of sodium was tried upon fumaric ester.



(V)

Due to the very poor yield of compound (V) which did not respond to any test for unsaturation, the isolation of aspartic acid from it by hydrolysis could not be successfully effected, though an attempt was made in that direction. Citraconic ester similarly adds up urethane to yield urethanylmethyl succinic ester (VI).

By analogy, the action of acetamide, propionamide, benzamide and phthalamide, all of which form sodium derivatives, was similarly studied upon cinnamic ester with the result that both acetamide and propionamide were found to react with the ester yielding cinnamic acid amide. The reaction evidently takes the following course.

$$Ph{\cdot}CH{=}CH{\cdot}CO_2Et + NaNH{\cdot}CO_2Me \longrightarrow PhCH{=}CH{\cdot}CO{\cdot}NH{\cdot}CO_2Me$$
$$\xrightarrow{\text{Hydrolysis}} PhCH{=}CH{\cdot}CO{\cdot}NH_2 \quad \text{(VII)}$$

Benzamide and phthalamide do not react at all.

Part II.

Seeing that urethane adds up to the double bond of unsaturated acid esters, it was thought worth-while to study the action of urethane upon unsaturated compounds like *iso*cyanates and thiocarbimides. The action of acetoacetic and malonic esters upon thiocarbimides has been studied by Worrall (*J. Amer. Chem. Soc.*, 1920, **42**, 1055 ; 1922, **44**, 1551 ; 1923, **45**, 3092 ; 1924, **46**, 2832 ; 1928, **50**, 1456).

Phenyl*iso*cyanate reacts readily with urethane to yield sodium derivative of carbethoxyphenylurea, thus :

$$\begin{matrix} PhN{=}C{=}O \\ + \\ NaNH{\cdot}CO_2Et \end{matrix} \longrightarrow \begin{matrix} PhN{-}CO \\ | \quad | \\ Na \ NH{\cdot}CO_2Et \end{matrix} \xrightarrow{\text{Acid}} \underset{\text{(VIII)}}{Ph{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO_2Et}$$

Phenylthiocarbimide reacts with urethane to give a compound (m.p. 248°) and possessing the composition $C_{15}H_{11}ON_3S_2$ (Found : N, 13·57 ; S, 20·14 per cent.) whereas the expected carbethoxyphenylthiourea (m.p. 130°, Doran, *J. Chem. Soc.*, 1896, **69**, 326) requires N, 12·50 and S, 14·22 per cent. Evidently the reaction takes a different course. Mustard oils are well known to react with thiocarbamides and dithiocarbazinic acids and their derivatives to form ring-closed compounds (Busch and Wolpert, *Ber.*, 1901, **34**, 304). By analogy with this sort of behaviour of mustard oils, the formation of the compound (m.p. 248°) can be explained on the assumption that the expected carbethoxyphenylthiourea, as soon as it is formed, reacts with

another molecule of mustard oil to yield a triazine compound, thus:

$$Ph{\cdot}N{:}C{:}S + NH_2{\cdot}CO_2Et \xrightarrow{Na} PhNH{\cdot}CS{\cdot}NH{\cdot}CO_2Et$$

$$PhNH{-}CS{-}NH{-}CO_2Et + S{:}C{:}NPh \rightarrow \underset{(IX)}{PhN{-}CS{-}NH \\ SC{\cdot}NPh{-}CO} \quad \text{or} \quad \underset{(IXa)}{PhN{-}CS{-}NH \\ PhN{:}C{-}S{-}CO}$$

The alternative formula (IX*a*) has been rejected because of the fact that from the methylthiol-derivative of the compound one atom of sulphur can be removed as mercuric sulphide, on treatment with red oxide of mercury in alcoholic solution—which shows that the second sulphur atom is not present in the molecule as a member of the ring (as in IX*a*) but it is present in the thioketonic form (as in IX) (*vide* Busch, *Ber.*, 1901, **34**, 304; Guha, *J. Amer. Chem. Soc.*, 1922, **44**, 1502). That the reaction actually takes the course as indicated above has been proved by condensing carbethoxyphenylthiourea (prepared by Doran's method, *loc. cit.*) with phenyl mustard oil when a compound identical with (IX) is obtained. Similar compounds (X, XI, and XII) have been obtained with *o*-tolyl, *m*-tolyl, and 1 : 3 : 4-xylyl mustard oils and they have all been shown to be identical with compounds prepared from the corresponding carbethoxythioureas prepared by Doran's method (*loc. cit.*) and mustard oils. This method of condensing mustard oils with carbethoxythioureas has been utilised for the preparation of isomeric triazine compounds (type IX) *e.g.*, carbethoxyphenylthiourea and *o*-tolyl mustard oil give a compound different from but isomeric with that obtained from carbethoxy-*o*-tolylthiourea and phenyl mustard oil. Compounds (XVII, XVIII, XIX, XX) have been similarly obtained by condensing carbethoxy derivatives of *p*-tolylthiourea with phenyl, *o*-tolyl and allyl mustard oils and carbethoxy-*o*-tolylthiourea with allyl mustard oil.

$$\underset{(XVII)}{p\text{-}C_7H_7{\cdot}N{-}\underset{CS{-}NPh{\cdot}CO}{CS{-}NH}} \qquad \underset{(XVIII)}{p\text{-}C_7H_7{\cdot}N{-}\underset{CS{-}N(o\text{-}C_7H_7){-}CO}{CS{-}NH}}$$

$$\underset{(XIX)}{p\text{-}C_7H_7{\cdot}N{-}\underset{CS{\cdot}N(C_3H_5){-}CO}{CS{-}NH}} \qquad \underset{(XX)}{o\text{-}C_7H_7{\cdot}N{-}\underset{CS{\cdot}(N{\cdot}C_3H_5){-}CO}{CS{-}NH}}$$

The behaviour of allyl mustard oil in its reaction with urethane appears to be different from that observed with the aromatic musturd oils described above—in so far as it gives the corresponding carbethoxythiourea which when separately treated with another molecule of allyl mustard oil gives the diallyl substituted triazine compound. It is to be mentioned here that in the case of the aromatic mustard oils the triazine compounds are formed irrespective of the quantity of mustard oils taken. Carbethoxyphenylurea $PhNH{\cdot}CO{\cdot}NH{\cdot}CO_2Et$, however, has been found to possess no capacity for reacting further with mustard oils and *iso*cyanates to yield triazine compounds as the corresponding carbethoxythioureas always do.

The preparation of thiocarbonyldiurethane, $CS(NHCO_2Et)_2$(XXI) has now been attempted by condensing carbethoxythiocarbimide with urethane in presence of sodium and dry ether. The expected sodium derivative of thiocarbonyldiurethane on acidification, was found to decompose into carbon dioxide, alcohol and other products. It, however, gives a stable copper derivative which has been analysed.

Experimental.

β-Urethanylphenylpropionic Ester (I).—Sodium (1·2 g.) was put into a solution of urethane (4·5 g.) in absolute ether (150 c.c.). Hydrogen began to evolve profusely for about 2 hours and a white precipitate (sodium derivative of urethane) came down. To this ethyl cinnamate (8·8 g.) was then added and the reaction mixture allowed to stand overnight. Next morning the precipitate was filtered, washed with ether and absolute alcohol and then dissolved in water. The aqueous solution, on being treated with dilute hydrochloric acid, gave a white precipitate which crystallised from dilute alcohol in colourless prismatic needles, m.p. 70°. It does not decolourise bromine water. (Found: N, 4·83. $C_{14}H_{19}O_4N$ requires N, 5·28 per cent.).

β-Urethanyl-o-nitrophenylpropionic Ester (II).—The method of preparation was the same as in the case of compound (I). The compound was crystallised from alcohol, m.p. 210°. (Found: N, 8·81. $C_{14}H_{18}O_4N_2$ requires N, 9·03 per cent.).

β-Urethanyl-m-nitrophenylpropionic Ester (III).—It was crystallised from alcohol, m.p. 195°. (Found: N, 8·74. $C_{14}H_{18}O_4N_2$ requires N, 9·03 per cent.).

β-Urethanyl-p-nitrophenylpropionic Ester (IV).—The substance was crystallised from alcohol, m.p. above 280°. (Found: N, 8·79. $C_{14}H_{18}O_4N_2$ requires N, 9·03 per cent.).

Hydrolysis of Compound (I).—The compound (I) was heated with 5 per cent. caustic potash solution under reflux on the water-bath for about an hour. The clear colourless solution, when cold, was acidified with dilute hydrochloric acid when a shining colourless crystalline mass came down. It was found to melt at 132-133° after crystallisation from hot water and was identified to be cinnamic acid by taking the mixed melting point with a genuine sample. The hydrolysis can also be effected with 2*N*-hydrochloric acid.

Action of Urethane on Methyl Fumarate: Formation of N-Carbethoxyaspartic Ester (V).—The method of procedure was the same as in the case of the preceding compound (I). The copper derivative was obtained by adding a concentrated solution of copper acetate and this gave the free urethanyl compound on acidification and extraction with ether. The solid obtained from the ethereal extract on evaporation crystallised from boiling water, m.p. 130° (shrinks at 110°). (Found: N, 5·54. $C_9H_{15}O_6N$ requires N, 6·01 per cent.). The yield of this substance was too poor to allow hydrolysis being studied.

Urethanylmethylsuccinic Ester (VI).—Citraconic ester (9·3 g.) was added to an ethereal suspension of sodiourethane prepared from urethane (4·5 g.) and sodium (1·2 g.) and the reaction mixture allowed to stand overnight. Next morning, a fine yellow solid was obtained which after filtration and washing with dry ether was found to get coloured on exposure to air. So it was quickly dissolved in water and the copper derivative was obtained as a greenish mass by adding a concentrated solution of copper acetate. The copper derivative, however, seemed to be quite stable. The free urethanyl compound was generated from its copper derivative by shaking an ethereal suspension of the latter with dilute sulphuric acid. The ethereal layer after being dehydrated over anhydrous magnesium sulphate was evaporated to dryness. The heavy brownish liquid thus obtained showed no tendency towards solidification even when kept in vacuum for a long time. (Found: N, 4·62. $C_{12}H_{21}O_6N$ requires N, 5·09 per cent.).

Action of Urethane on Mesaconic Ester: Formation of Urethanylmethylsuccinic Ester (VI*a*).—The method of procedure was the same as in the case of the preceding compound (VI). The brownish red heavy liquid obtained from the copper derivative on acidification

could not be solidified even on long standing in vacuum over sulphuric acid. (Found: N, 4·64. $C_{12}H_{21}O_6N$ requires N, 5·09 per cent.).

Action of Acetamide on Cinnamic Ester: Formation of Cinnamamide (VII).—Sodium (1·2 g.) was gradually added to a solution of acetamide (3 g.) in absolute ether (120 c.c.). The evolution of hydrogen ceased after about two hours when the sodium derivative of acetamide separated as a white precipitate. The mixture after the addition of ethyl cinnamate (9 g.) was allowed to stand overnight. Next morning the separated orange-yellow solid was dissolved in water and acidified with dilute hydrochloric acid when a solid mixed with some tarry matter was obtained. On boiling with water the solid went into solution leaving behind the tarry matter and the filtrate after treatment with animal charcoal and concentration yielded white shining plates, m.p. 142-143°. It is readily soluble in alcohol, acetic acid but sparingly so in benzene. It is soluble in strong hydrochloric acid but not in alkali. (Found: N, 9·26. C_9H_9ON requires N, 9·52 per cent.). The compound decolourises bromine water and the isolated bromo-derivative melts at 200° (decomp.).

The action of propionamide on cinnamic ester was similarly tried and the resulting compound (m.p. 142-143°) was proved to be cinnamamide by taking the mixed melting point with the product obtained in the preceding experiment as also by hydrolysing it with 2*N*-sodium hydroxide solution when cinnamic acid was obtained.

Carbethoxyphenylcarbamide (VIII).—Phenyl*iso*cyanate (6 g.) was added to an ethereal suspension of sodiourethane obtained from sodium (1·2 g.) and urethane (4·5 g.). The reaction at once started and the mixture was allowed to stand overnight. The white precipitate thus obtained was dissolved in water and acidified with dilute hydrochloric acid when a colourless precipitate came down which crystallised from alcohol in beautiful, colourless, plates, m.p. 106-107°. (Found: N, 13·57. $C_{10}H_{12}O_3N_2$ requires N, 13·46 per cent.).

1:5-Diphenyl-2:6-dithion-4-ketohexahydro-1:3:5-triazine (IX).—Phenyl mustard oil (7 g.) was added to an ethereal suspension of sodiourethane obtained from sodium (1·2 g.) and urethane (4·5 g.), and the mixture allowed to stand overnight. The yellow precipitate thus obtained was dissolved in water and acidified with dilute hydrochloric acid. The precipitated semi-solid mass was purified by dissolving it in ether and precipitating by means of petroleum ether and finally crystallising from methyl alcohol in beautiful, yellow, rectan-

gular prisms, m.p. 248°. (Found: N, 13·57; S, 20·14. $C_{15}H_{11}OS_2N_3$ requires N, 13·41; S, 20·44 per cent.). It is soluble in cold alkali from which it is precipitated by acids. It is decomposed on boiling with dilute alkali.

The *monomethyl* derivative was obtained by dissolving compound (IX) in the minimum quantity of caustic soda solution and boiling the solution with the requisite quantity of methyl iodide in presence of alcohol for about 15 minutes when colourless crystals came out. These were recrystallised from alcohol in shining, hexagonal prisms, m.p. 220°. (Found: N, 12·53. $C_{16}H_{13}OS_2N_3$ requires N, 12·84 per cent.).

The *benzoyl* derivative was obtained by Schotten-Baumann process and was crystallised from alcohol in shining colourless prisms, m.p. 158—159°. The *bromo-derivative* was obtained by dissolving the compound (IX) in glacial acetic acid and adding bromine water. The precipitate was crystallised from alcohol, m.p. 200° (after shrinking and softening at 140°).

Action of Red Oxide of Mercury on the above Methyl Derivative: *Formation of* 1:5-*Diphenyl*-2-*methylthiol*-4:6-*diketohexahydro*-1:3:5-*triazine*.—The monomethyl derivative of compound (IX) in alcoholic solution was boiled with an excess of mercuric oxide which turned black due to its conversion into mercuric sulphide. The alcoholic filtrate on evaporation to dryness left a white solid which crystallised from alcohol in shining, colourless plates, m. p. 195°. (Found : N, 13·18. $C_{16}H_{13}O_2SN_3$ requires N, 13·50 per cent.).

1:5-*Di*-o-*tolyl*-2:6-*dithion*-4-*ketohexahydro*-1:3:5-*triazine* (X).—The method of procedure was the same as in the case of the preceding compound (IX). It was crystallised from methyl alcohol in yellow, rectangular prisms, m. p. 280°. It is soluble in cold alkali from which it is precipitated by acids. (Found: N, 12·00 ; S, 18·50 ; C, 59·41 ; H, 4·88. $C_{17}H_{15}OS_2N_3$ requires N, 12·31 ; S, 18·76 ; C, 59·82 ; H, 4·39 per cent.).

1:5-*Di*-m-*tolyl*-2:6-*dithion*-4-*ketohexahydro*-1:3:5-*triazine* (XI).—The method of procedure was the same as in the case of the phenyl and o-tolyl compounds. It crystallised from methyl alcohol in yellow, rectangular prisms, m.p. 237° (after shrinking at 226°). It is soluble in cold alkali from which is pricipitated by acids. (Found: N, 12·12. $C_{17}H_{15}OS_2N_3$ requires N, 12·31 per cent.).

1:5-Dixylyl-2:6-dithion-4-ketohexahydro-1:3:5-triazine (XII).—was prepared similarly from sodiourethane and 1:3:4-xylyl mustard oil and, after effecting the precipitation with petrol from ethereal solution, was crystallised from dilute alcohol, m. p. 223-225°. It is soluble in cold alkali from which it is precipitated by acids. (Found: N, 10·94. $C_{19}H_{19}OS_2N_3$ requires N, 11·38 per cent.).

3-Carbethoxy-1-allylthiourea, $C_3H_5NH{\cdot}CS{\cdot}NH{\cdot}CO_2Et$ (XIII).—Molecular proportions of sodiourethane and allyl mustard oil were allowed to stand in presence of dry ether for 24 hours. The precipitated sodium derivative after filtration and washing was dissolved in water and acidified with dilute hydrochloric acid. The semi-solid white mass that came down was purified by dissolving it in dilute sodium hydroxide solution and reprecipitating with dilute hydrochloric acid. It was finally crystallised from alcohol in colourless, rectangular plates, m. p. 57°. (Found: N, 15·06 ; S, 16·61. $C_7H_{12}O_2SN_2$ requires N, 14·89 ; S, 17·02 per cent.).

1:5-Diallyl-2:6-dithion-4-ketohexahydro-1:3:5-triazine (XIV).—Sodium (1·2 g.) was dissolved in a solution of carbethoxyallylthiocarbamide (9·4 g.) dissolved in 156 c.c. of absolute ether. Hydrogen began to evolve profusely for about two hours during which period the sodium derivative went on being gradually deposited as a white precipitate. The reaction mixture, after the addition of allyl mustard oil (10 g.) to it, was allowed to stand overnight. Next morning the reaction mixture was found to be free from any smell of allyl mustard oil and the precipitate that had separated out was dissolved in water and acidified with dilute hydrochloric acid. The precipitate was purified by dissolving it in ether and shaking with sodium carbonate solution. The alkaline solution on being acidified with dilute hydrochloric acid, yielded a precipitate which crystallised readily from alcohol, m. p. 133°. (Found: N, 17·14. $C_9H_{11}OS_2N_3$ requires N, 17·42 per cent.).

1:5-Diphenyl-2:6-dithion-4-ketohexahydro-1:3:5-triazine (IX).—Sodium (1 g.) was added to a solution of carbethoxyphenylthiocarbamide (10 g.) in dry ether (120 c.c.). After about two hours, when all the sodium has reacted, phenyl mustard oil (6 g.) was added and the mixture allowed to stand overnight. The aqueous solution of the separated solid on acidification with dilute hydrochloric acid yielded a yellow precipitate which was disolved in ether and shaken with a solution of sodium carbonate. The alkaline solution, on acidification gave a precipitate which crystallised readily from methyl

alcohol in beautiful, yellow, rectangular prisms, m. p. 248°. (Found N, 13·12. $C_{15}H_{11}OS_2N_3$ requires N, 13·41 per cent.). The identity of this compound with (IX) was confirmed by taking a mixed melting point.

Action of Carbethoxyphenylthiourea upon o-*Tolyl Mustard Oil* : *Formation of* 1-*Phenyl*-5-o-*tolyl*-2 : 6-*dithion*-4-*ketohexahydro*-1 : 3 : 5-*triazine* (XV).—The method of preparation and purification was the same as in the case of the compound (IX). The compound was crystallised from methyl alcohol in rectangular prisms, m. p. 244°-245°. It gives insoluble mercury and lead salts with mercuric chloride and lead acetate solutions respectively. (Found : N, 12·67. $C_{16}H_{13}OS_2N_3$ requires N, 12·84 per cent.). The *benzoyl* derivative crystallised from alcohol in colourless, shining prisms, m. p. 205°.

Action of Carbethoxy-o-*tolylthiocarbamide upon Phenyl Mustard Oil*: *Formation of* 1-o-*Tolyl*-5-*phenyl*-2 : 6-*dithion*-4-*ketohexahydro*-1 : 3 : 5-*triazine* (XVI).—The method of procedure was the same as in the case of the compound (XV). The yellow precipitate obtained from the sodium carbonate solution crystallised from methyl alcohol in rectangular prisms, m. p. 235°-236°. (Found : N, 12·72. $C_{16}H_{13}OS_2N_3$ requires N, 12·84 per cent.). The *benzoyl* derivative was crystallised from alcohol, m. p. 155°.

Action of Carbethoxy-p-*tolylthiocarbamide upon Phenyl Mustard Oil*: *Formation of* 1-p-*Tolyl*-5-*phenyl*-2 : 6-*dithion*-4-*ketohexahydro*-1 : 3 : 5-*triazine* (XVII).—The method of procedure was the same as in the case of the compound (XV). The yellow precipitate was crystallised from methyl alcohol, m. p. 251-252°. (Found : N, 12·61. $C_{16}H_{13}OS_2N_3$ requires N, 12·84 per cent.).

Action of Carbethoxy-p-*tolylthiocarbamide upon* o-*Tolyl Mustard Oil*: *Formation of* 1-p-*Tolyl*-5-o-*tolyl*-2 : 6-*dithion*-4-*ketohexahydro*-1 : 3 : 5-*triazine* (XVIII).—The method of preparation was the same as in the case of the compound (XV). It was obtained in yellow rectangular prisms from methyl alcohol, m. p. 224°. (Found : N, 12·09. $C_{17}H_{15}OS_2N_3$ requires N, 12·31 per cent.).

Action of Carbethoxy-p-*tolylthiocarbamide upon Allyl Mustard Oil*: *Formation of* 1-p-*Tolyl*-5-*allyl*-2 : 6-*dithion*-4-*ketohexahydro*-1 : 3 : 5-*triazine* (XIX).—The substance was crystallised from alcohol, m. p. 145°. (Found : N, 14·12. $C_{13}H_{13}OS_2N_3$ requires N, 14·43 per cent.)

Action of Carbethoxy-o-tolylthiocarbamide upon Allyl Mustard Oil: Formation of 1-o-*Tolyl-5-allyl-2:6-dithion-4-ketohexahydro-1:3:5-triazine* (XX).—It was crystallised from alcohol, m. p. 136-137°. (Found: N, 14·21. $C_{13}H_{13}OS_2N_3$ requires N, 14·43 per cent.).

Thiocarbonyl diurethane (XXI).—Carbethoxythiocarbimide (6·6 g.) prepared according to the method of Doran, (*loc.cit.*) and dissolved in toluene was added to a toluene suspension of sodiourethane obtained from sodium (1·2 g.) and urethane (4·5 g.) and the mixture allowed to stand overnight. Next morning the precipitate thus obtained was dissolved in water and acidified with dilute hydrochloric acid in an ice-cold bath when carbon dioxide began to evolve profusely and a reddish-brown tarry matter was obtained. The *copper* derivative was, however, obtained by adding a concentrated solution of copper acetate to the aqueous solution of the sodium derivative and a brownish-white precipitate was obtained, which was washed with alcohol, water and dried. (Found: N, 11·14. $(C_7H_{11}O_4SN_2)_2Cu$ requires N, 11·16 per cent.). The copper derivative also decomposes on the addition of acids.

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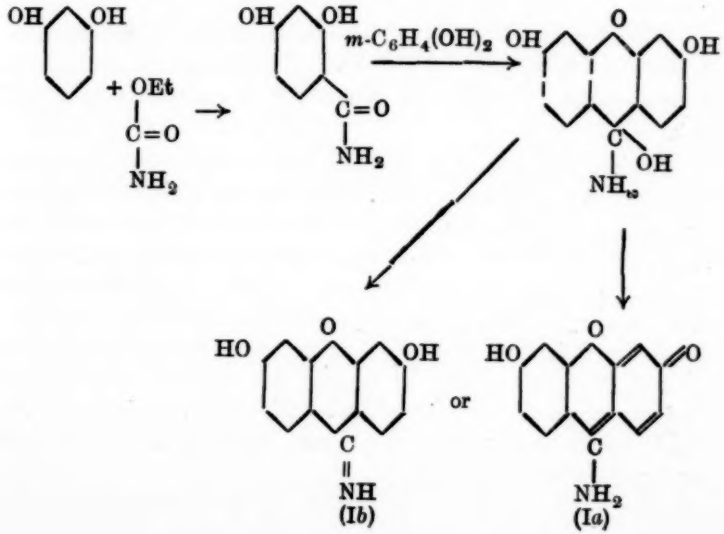
Condensations of Urethane, Phenylurethane and Diphenylurethane with Resorcinol.

By Rajendra Nath Sen and Ashutosh Mukherji.

Sen and Guha-Sarkar succeeded in bringing about a condensation of salicylic ester with resorcinol and pyrogallol with the formation of benzeins (*J. Indian Chem. Soc.*, 1924, **1**, 157). In elaboration of that work, Sen and Mukherji (*J. Indian Chem. Soc.*, 1929, **6**, 557) successfully condensed resorcinol, dimethylaniline and diethyl-*m*-aminophenol with various aromatic and aliphatic esters and glycerides.

In the present investigation, the same reaction has been further extended to the condensation of urethane and substituted urethanes with resorcinol leading to the formation of pyronine dyes in which the hydrogen-atom attached to the central carbon atom has been replaced by an amino- or a substituted amino-group, the mechanism of the reaction being represented thus:—



The structure (I*a*) for the urethane condensation product is supported by the following observations:—

(*a*) The compound gives coloured mono-potassium and mono-silver salts.

(*b*) When acetylated in alkaline solution by chloroacetyl chloride, it yields a monochloracetyl derivative (only hydroxyl attacked). Structure (I*b*) should have given a dichloroacetyl derivative.

(*c*) When acetylation is carried out by heating the compound with chloroacetyl chloride at its boiling point, a dichloroacetyl compound is formed (OH and NH_2 both attacked). Structure (I*b*) should have given a trichloracetyl derivative.

(*d*) When to a hot solution of the compound in alcohol mixed with a solution of sodium nitrite, dilute hydrochloric acid is dropped, nitrogen is evolved and the product that is formed is found to be free from nitrogen and on further crystallization from alcohol melts at 235° and is probably the expected *iso*euxanthone (m.p. 243°).

It is remarkable that alkaline or acid hydrolytic agents such as alcoholic potash, strong hydrochloric acid or moderately strong sulphuric acid have no action on the compound, showing that the NH_2-group in this configuration is quite stable. It may also be noted that the compound is insoluble in dilute acids.

When brominated, the urethane compound yields a tetrabromo-derivative, while the phenyl and diphenyl compounds yield dibromo-derivatives, all of which dye beautiful red shades on wool and silk.

In alkaline and alcoholic solutions, the condensation products of resorcinol with urethane and substituted urethanes exhibit moderate fluorescence (bluish-green), which is most marked in the case of the unsubstituted product. The urethane compound dyes golden yellow shade on wool and silk, which becomes slightly deeper (redder) as the hydrogen atoms in urethane are substituted by phenyl residues. Since the difference in the colour of the compounds is not more marked, the urethane and the monophenyl urethane condensation products appear also to have a quinonoid structure (I*a*), like the diphenylurethane condensation product which admits of no other configuration but the quinonoid.

Experimental.

6-Hydroxy-9-aminofluorone (Ia).—Urethane (1 mol.) and resorcinol (2 mols.) were heated to 180° for 6 hours with zinc chloride as the condensing agent. The product was purified in the same way as resorcinolbenzein (*J. Indian Chem. Soc.*, 1926, **6**, 557). It is a brownish-yellow powder, soluble in alcohol, acetone, glacial acetic acid, less so in benzene, ether and chloroform; insoluble in petroleum ether and toluene. Alkaline alcoholic and acetone solutions show green fluorescence. It dyes golden yellow shades on wool and silk and softens at 210° ; yield 85 per cent. (Found: N, 5·95. $C_{13}H_9ON_3$ requires, N, 6·16 per cent.).

Monopotassium Derivative.—Prepared as usual. (Found: K, 14·7. $C_{13}H_8O_3NK$ requires K, 14·7 per cent.).

Monosilver derivative.—Prepared from the K-derivative by the addition of silver nitrate. (Found: Ag, 32·2. $C_{13}H_8O_3NAg$ requires Ag, 32·3 per cent.).

Monochloracetyl Derivative.—Prepared by shaking the alkaline solution with the addition of chloracetyl chloride drop by drop till acid. Recrystallised from glacial acetic acid, it softens at 194°. (Found: Cl, 11·55. $C_{15}H_{10}O_4NCl$ requires Cl, 11·69 per cent.).

Dichloracetyl Derivative.—Prepared by boiling 6-hydroxy-9-aminofluorone with excess of chloracetyl chloride under an air condenser. Purified from alcohol and then from glacial acetic acid m.p. 150°. (Found: Cl, 18·20. $C_{17}H_{11}O_5NCl_2$ requires Cl, 18·70 per cent).

Tetrabromo Derivative.—Prepared by bromination in alcoholic solution and recrystallisation from alcohol. It decompose at 250°. (Found: Br, 57·9. $C_{13}H_5O_3NBr_4$ requires Br, 58·9 per cent.).

6-Hydroxy 9-phenylaminofluorone.—Prepared from phenylurethane and resorcinol. Brownish-yellow powder. Softens at 195°. Solubility similar to 6-hydroxy-9-aminofluorone. Dyes slightly redder shades. Alkaline and alcoholic solutions show bluish-green fluorescence. Yield 80%, (Found: N, 4·5. $C_{19}H_{13}O_3N$ requires N, 4·62 per cent.).

Dibromo-derivative.—Prepared by brominating the above. Red powder decomposing at 290°. Dyes wool and silk red shades.

6-Hydroxy-9-Iphenylaminofluorone.—Prepared from diphenyl urethane and resorcinol. Brownish-yellow powder softens at 275°. Dyes wool and silk reddish-brown shades. Alkaline and alcoholic solutions show blue fluorescence. Yield 80 per cent. (Found: N, 3·59. $C_{25}H_{17}O_3N$ requires N, 3·69 per cent.).

Dibromo-derivative$_2$—Prepared by brominating the above compound in alcoholic solution. Red powder, decomposes at 220°. Dyes wool and silk bright red shades. (Found: Br, 29·4. $C_{25}H_{15}O_3NBr_2$ requires Br, 29·9 per cent.).

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The Catechins of the Cutch-producing Acacias.

By M. Nierenstein.

Singh (*Indian Forest Memoirs*, 1905, **1**, 34) was the first to draw attention to the differences in the melting points of catechin from cutch (m.p. 195-198°), and kheersal (m.p. 225-230°), the catechin found in the heart-wood of *Acacia Catechu*. Sixteen years later Freudenberg and Purrmann (*Annalen*, 1924, **437**, 278) showed that the heart-wood of *A. Catechu* contained mainly *l*-epicatechin (m.p. 230°), and also some *dl*-catechin (m.p. 212°). According to Freudenberg and Purrmann *l*-epicatechin undergoes epimerisation and racemisation, during the manufacture of cutch, *dl*-catechin (m.p. 212°) being produced. From nearly thirty years' experience with catechin the present writer is inclined to believe that the variations between Singh's melting points and those given by Freudenberg and Purrmann for the catechin found in the wood and that in the cutch, are within the limits of experimental error, an opinion which would appear to be corroborated by the variation in melting points of *dl*-catechin alone—216-18°, 214-16°, 204-5°, 212-14°, and 212°, recorded by Freudenberg and his collaborators. The melting points of the different catechins are greatly affected by moisture—a point which has been particularly emphasised in the case of gambier-catechin (see Kostanecki and Tambor, *Ber.*, 1902, **35**, 1867; Clauser, *ibid.*, 1903, **36**, 101; Perkin, *J. Chem. Soc.*, 1905, **87**, 398) which melts at 96°, 175-77°, and 210° respectively, these variations being due to the water of crystallisation. For this reason the author prefers the different penta-acetyl derivatives, for identification purposes as these crystallise with ease from alcohol and have constant melting points. In view of these considerations no doubt remains that to Singh belongs the credit of having discovered the native catechin of *A. Catechu*.

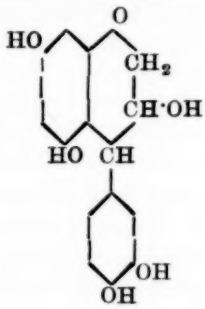
According to Freudenberg and Purrmann the first stage in the conversion of kheersal (mainly *l*-epicatechin) into *dl*-catechin (known in the literature as acacatechin), consists in the epimerisation of *l*-epicatechin to *l*-catechin which is followed by the second stage, namely, the racemisation of *l*-catechin to *dl*-catechin (acacatechin).

On heating an aqueous solution of *l*-epicatechin under pressure Freudenberg and Purrmann obtained a mixture of four catechins, namely, *l*-epicatechin, *l*-catechin, *dl*-epicatechin, and *dl*-catechin; and further, they demonstrated that the reaction is reversible, since, starting out from *l*-catechin and working under the same conditions, they obtained *l*-catechin, *l*-epicatechin, *dl*-catechin, *dl*-epicatechin.

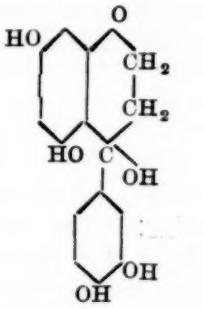
A clear understanding of these reactions, the extent to which they take place, possible variations of yields, and of the factors controlling these, is obviously fundamental to the chemistry of cutch, and at the writer's request therefore Miss Edith O. Hazelton repeated Freudenberg's experiment on a large scale, with the single difference that whereas Freudenberg and Purrmann had started from *l*-catechin or *l*-epicatechin respectively, and obtained a mixture of four catechins, Miss Hazelton started from *dl*-catechin, which, on epimerisation could only lead to a mixture of two catechins, namely, *dl*-catechin and *dl*-epicatechin.

The collective evidence of Miss Hazelton's experiments, full details of which are given in the experimental part of this paper, revealed however no trace of epimerised catechin. Furthermore, simple considerations of Freudenberg and Purrmann's discovery in *A. Catechu* of *dl*-catechin, as well as *l*-epicatechin, the main constituent of the heart-wood suggest only one explanation, which is hard to realise, namely, that in the plant, *l*-epicatechin is epimerised, as well as racemised, at the exclusion of *dl*-epicatechin leading to the production of *dl*-catechin. At one time during the progress of the present investigation it was thought that evidence had accumulated showing the presence of *dl*-epicatechin in the wood, since *three* catechins were found in the heart-wood, namely, α-catechin, (m.p. 204-5°), β-catechin (m.p. 230°) and γ-catechin (m.p. 226-8°), yielding the corresponding penta-acetyl derivatives, having melting points 160°, 151°, and 171° respectively. However subsequent work has shown that only two of these catechins are stereoisomers, that is to say β-catechin, which is laevo-rotatory, can be racemised to α-catechin, *viz.*, acacatechin (Nierenstein, *J. Chem. Soc.*, 1921, **119**, 164) whereas γ-catechin, which is also laevo-rotatory, is a structural isomer of α- and β-catechin, since it can be racemised to *iso*acacatechin (Nierenstein, *Ber.*, 1923, **56**, 1877). The following names have therefore been provisionally assigned to these three catechins, *dl*-acacatechin (m.p. 204-5°; acetyl derivative, m.p. 160°), *l*-acacatechin (m.p. 230°; acetyl derivative, m.p. 151°), and *l-iso*acacatechin

(m.p. 226-8°; acetyl derivative, m.p. 171°). The constitution of acacatechin is shown in formula I, whereas formula II represents the constitution of *iso*acacatechin.



(I)



(II)

The results obtained in this laboratory go to show that—(1) During the manufacture of cutch the greater part of the catechin is destroyed, thus the ethyl acetate extracts obtained on exhaustive extraction of the heart-wood as well as of the cutches prepared from the same wood, are found to give the following comparative catechin values on exhaustive extraction with ether:

	Catechin content.	
	Wood.	*Cutch.*
Acacia Catechu, Log A.	58·00%	14·75%
Acacia Catechu, Log B.	62·40%	10·40%
Acacia Catechu, Log C.	70·00%	32·00%
Acacia Sundra.	61·00%	38·30%
Acacia Catechuoides.	59·00%	25·10%

(2) Racemisation of the two optically active catechins takes place to some extent, but is erratic, and far from being complete. This is shown in the following summary:—

	Heart-wood.			*Cutch.*		
	dl-Acacatechin.	*l*-Acacatechin.	*l-iso*Acacatechin.	*dl*-Acacatechin.	*l*-Acacatechin.	*l-iso*Acacatechin.
Acacia Catechu, Log A.	13·84%	51·70%	32·93%	77·00%	—	23·00%
Acacia Catechu, Log B.	13·57%	76·98%	9·45%	51·2%	—	48·60%
Acacia Catechu, Log C.	22·40%	74·20%	3·40%	13·40%	72·10%	14·50%
Acacia Sundra	3·10%	94·30%	2·60%	—	100·0%	—
Acacia Catechuoides	22·70%	73·90%	3·40%	45·90%	48·40%	4·1%

It will be realised that it is quite impossible to generalise from these results, or to use them in support of any theory of the mechanism of cutch production from catechin. Only a large number of experiments, preferably carried out in India, will elucidate the points raised by this preliminary work.

Experimental.

The wood as well as the cutches was exhaustively extracted with ethyl acetate in a large Soxhlet apparatus. The cutches were finely powdered, passed through a 30-sieve and mixed with ten times their own weight of white sand.* The ethyl acetate extracts were evaporated to dryness under reduced pressure and the remaining solid powdered and again mixed with ten times its own weight of sand. It was then fractionally extracted in a Soxhlet apparatus with ether free from alcohol. The first fraction was obtained after thirty minutes' extraction and the time of extraction increased for each subsequent fraction. Extraction was continued until no solid was obtained on evaporation of the ether. The average time of extraction totalled 200 hours. The solids obtained on evaporation of the ether were dissolved in hot water slightly acidulated with acetic acid (see Nierenstein, *J. Chem. Soc.*, 1922, **121**, 609) and the solid collected after standing for twenty-four hours. The catechin fractions thus obtained were again recrystallised from water and the weight of each fraction and its melting point recorded after standing in a vacuum desiccator over concentrated sulphuric acid for 3—5 days. Each fraction was then acetylated by heating with acetic anhydride and the solid obtained on precipitation with water crystallised from alcohol and a few drops of acetone. The melting point and the mixed melting point with specially purified authentic specimens were recorded. The filtrates of the different fractions were all mixed together, and evaporated by standing over concentrated sulphuric acid, the solid thus obtained was powdered and mixed with sand, and again fractionally extracted with ether, and examined in the manner described above, the aqueous filtrates of these second fractions being solidified and examined in the same way. It was generally found that these third solids contained little or no catechin.

* The sand used was at first treated with a dilute hydrochloric acid, then washed with water, alcohol and ether. It was then dried at 100° and powdered.

The results obtained after this somewhat lengthy process have already been summarised in the introduction, and although they did not yield data which could lend themselves to the development of a theory as to the fate of catechin during the manufacture of cutch they may serve as a useful basis for other workers in this field.

As regards Miss Hazelton's results, which are summarised in the accompanying table, they were obtained as follows:—100 g. *dl*-acacatechin (m.p. 204-5°; acetyl derivative, m.p. 160°) were heated under pressure according to the conditions laid down by Freudenberg and Purrmann for the epimerisation of *l*-epicatechin. The crystalline remaining catechin was then filtered off and dried, the mother-liquor being carefully evaporated to a syrupy solution, when no further catechin crystallised out. The syrup was left to dry over sulphuric acid till it formed a solid. The solid obtained was powdered, and thoroughly mixed with the crystalline catechin which had been recovered, this mixture was then put through a 30-sieve, and left to dry in a desiccator over sulphuric acid for about a week. 50 G. of the cutch produced were examined in the manner already described.

The accompanying tables have been reproduced from the laboratory book of Miss Hazelton, who died at a very early age.

In conclusion, the author's thanks are due to the authorities of the Forest Research Institute at Dehra Dun, for their generosity in supplying the necessary material for this investigation.

TABLE I.

Ethereal Fractionation of Pure Acacatechin which has been heated under pressure. Fractions called " C "

No.	Time. (hrs.)	Weight of dish (g.)	Weight of residue and dish (g.)	Weight of Residue (g.)	Wt. of watch glass.	Weight of catechin and watch glass (g.)	Weight of catechin (g.)	Total weight (g.)	Melting point.	Acetyl derivative M.p.	Recryst. m.p.	Mixed m.p.
1	1	28·00	31·00	3·00	4·20	4·45	0·25	3·25	Sinters strongly at 160°. m.p. 200-202°	160°	...	160°
2	1½	34·80	38·10	3·30	5·00	6·00	1·00	4·30	204-205°	160°	...	160°
3	1¾	30·95	33·70	2·45	6·60	7·40	0·80	3·55	Sinters strongly at 160°; m.p. 201-203°	160°	...	160°
4	3	34·30	36·90	2·60	7·75	9·95	2·20	4·80	202-204°	155-157°	160°	160°
5	4½	28·00	30·10	2·10	11·20	13·40	2·20	4·80	202-204°	160°	...	160°
6	3½	34·80	41·10	6·30	13·70	16·40	2·70	9.00	200-202°	160°	...	160°
7	5	30·95	32·50	1·55	9·30	10·80	1·50	3·05	198-202°	160°	...	160°
8	6	34·30	35·05	0·75	12·10	14·05	1·95	2·70	204-205°	160°	...	160°
9	4½	34·80	35·20	0·40	14·30	15·95	1·65	2·05	203-205°	160°	...	160°
10	8	28·00	28·05	0·05	9·85	10·80	0·95	1·00	190-196°	160°	...	160°
11	9	30·95	31·05	0·10	5·00	5·90	0·90	1·00	198-200°	160°	...	160°
12	9	28·00	28·10	0·10	2·75	3·55	0·80	0·90	204-205°	160°	...	160°
13	13	30·95	31·00	0·05	10·05	10·50	0·45	0·50	203-205°	160°	...	160°
14	11	30·95	31·10	0·15	11·80	11·95	0·65	0·80	203-204°	160°	...	160°
15	14	28·00	28·05	0·05	7·30	7·65	0·35	0·40	202-204°	160°	...	160°
16	13	30·95	31·00	0·05	3·40	3·80	0·40	0·45	201-203°	160°	...	160°
17	14	36·50	36·60	0·10	11·00	11·65	0·65	0·75	202-203°	160°	...	160°
18	36½	33·45	33·50	0·05	No catechin			0·05		160°	...	160°
Total	158½			23·45			19·40	42·85				

2nd crystals to be found in table II.

TABLE II.

2nd Crystals C1A , etc.

No.	Wt. of watch glass (g.)	Wt. of catechin and watch glass(g.)	catechin (g.)	Melting point.	Acetyl derivative M.p.	Recrys. m.p.	Mixed m.p.
1A	7·85	8·40	0·55	160-165°	159-160°	160°	160°
2A	8·05	8·50	0·45	100-110°	110-125°, 150-158°	155-158°	155-160°
3A	9·80	10·00	0·20	157-160°	160°	...	160°
4A	2·80	3·90	0·10	202-204°	160°	...	160°
5A	1·45	1·55	0·10	199-200°	160°	...	160°
6A	2·95	3·10	0·15	160-163°	160°	...	160°
7A	No second crystals						
8A	1·50	1·60	0·10	198-200°	160°	...	160°
9A	1·65	1·75	0·10	195-198°	160°	...	160°
10A	9·70	9·80	0·10	194-198°	160°	...	160°
11A	7·85	7·95	0·10	190-196°	160°	...	160°
15A	9·60	9·85	0·25	201-203°	160°	...	160°
Residues							
6 hrs.	5·05	5·35	0·30	105-120°	157-160°	160°	160°
15 hrs.		No catechin					
		Total	2·50				

Total catechin 19·40 + 2·50 = 21·90 g. = 43·80%.

Total extract 4·285 + 2·20 = 45·05 g. = 90·1%.

43·80% *catechin* recovered and the whole of this amount was unchanged *aca catechin*. *No trace of epimerised substance.*

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Gravimetric Estimation of Potassium, Rubidium and Caesium by Zirconium Sulphate Method.

By N. A. Yajnik and G. L. Tandon.

A number of more or less satisfactory methods are available for the gravimetric estimation of potassium, the more important of which are platinum chloride (Clowes and Coleman, "Analytical Chemistry," 9th ed., p. 250), sodium hydrogen tartrate (Ajon. *Giorn. Chim. Ind. Appl.*, 1920, **2**, 422), perchloric acid (Hager and Kern, *Landw. Ver. Stat.*, 1915, **87**, 365), and sodium cobaltinitrite (Hamid, *Analyst*, 1926, **51**, 450) methods. Inspite of a large number of attempts made to improve these methods, a perusal of the literature shows that all these methods have their limitations in one respect or the other and none of these serve as a universal method.

Reed and Withrow (*J. Amer. Chem. Soc.*, 1928, **50**, 1515), as the result of a large number of qualitative experiments carried on by them, have shown that it is possible to detect, by the help of zirconium sulphate solution, even very low concentrations of potassium (0·5 mg.) from potassium sulphate solutions if no interfering ions are present. They have further shown that the sensitiveness of the zirconium sulphate test is as great as that of the sodium cobaltinitrite test provided that the solutions are allowed to stand for a longer time, in cold, after mixing. It has further been pointed out by the same workers that this test can also be used for the detection of potassium even in the presence of lithium, rubidium, caesium or magnesium (*J. Amer. Chem. Soc.*, 1929, **51**, 1062). This last observation appears rather an unusual one on the face of the observed and accepted similarity between the other properties of potassium, rubidium, and caesium. It is also contradictory to the previous work of Rosenheim and Frank (*Ber.*, 1905, **38**, 812) who showed that rubidium and caesium zirconyl sulphates could be prepared in exactly similar ways as the corresponding potassium salt. The reason why Reed and Withrow could not detect

the formation of these salts of rubidium and caesium was probably due to the fact that in their experiments, as compared to the amount of potassium salt taken, they had been using such small quantities of rubidium and caesium as would not have given any formation of the precipitate at the ordinary temperatures. Also, they had been using acidic solutions of the zirconium salt for their experiments, the use of which the authors have found to be detrimental to the precipitation of these double salts.

Taking into consideration the observations of Rosenheim and Frank, and Reed and Withrow, it appeared quite interesting to the authors to examine if it could be possible to utilise this method as one of the alternative methods for the gravimetric estimation of potassium, rubidium and caesium.

Moreover as Reed and Withrow were concerned with the qualitative side of the problem only, they never tried to ascertain the composition of the double compounds formed as the result of the reaction between potassium sulphate and zirconium sulphate. It appeared, therefore, also necessary to determine the exact condition under which complete reactions between the two solutions take place and the composition of the compound so formed.

Experimental.

(a) *The Preparation of Solutions.*

Zirconium sulphate solution.—22 G. of Merck's "extra pure" zirconium sulphate were heated in a porcelain crucible for 15 minutes on a blow-pipe flame. The heated substance was put in 100 c. c. of cold distilled water, stirred continuously for half an hour and finally filtered. This gave a saturated solution of the salt which was preserved in a clean glass-stoppered bottle. A fresh sample of the zirconium sulphate solution was prepared in a similar manner every day, since the solution undergoes hydrolysis on keeping for more than 48 hours.

Potassium, rubidium and caesium sulphate solutions were prepared in the usual way using Merck's "extra pure" substances.

Sodium cobaltinitrite solution was prepared by Hamid's method. (*loc. cit.*).

Potassium chloride and the perchloric acid solutions were prepared in the usual manner.

(b) *Determination of the Composition of the Double Salts formed and the Study of the Conditions under which they are obtained.*

A very large variety of the double salts of potassium with zirconium sulphate have been reported by various workers (Berzelius, Franz, Warren, Rosenheim and Frank, J. W. Mellor, "A Comprehensive Treaties on Inorganic Theoretical Chemistry, 1927, pp. 157-159; *Ber.*, 1905, **38**, 812) to have been obtained under varing conditions. Of all these reported compounds, the following three have the greatest stability and are easily prepared by the direct action of potassium sulphate (acid or normal) on the zirconium sulphate solution:—

(1) $3K_2O,3ZrO_2,7SO_3,9H_2O$, (2) $2K_2O,6ZrO_2,7SO_3,9H_2O$,

(3) $Zr_2O_3(KSO_4)_2,8H_2O$

while the rest of them are comparatively less stable and more difficult to prepare. Hence on account of these advantages only these compounds were studied.

As a result of a large number of preliminary experiments it was noticed that the compound $3K_2O,3ZrO_2,7SO_3,9H_2O$, was obtained by the action of an acidified solution of zirconium sulphate on acid potassium sulphate, while the compound $2K_2O,6ZrO_2,7SO_3,9H_2O$ was obtained when normal potassium sulphate was used. However, these compounds are not suitable for the gravimetric estimation of potassium, since they are fairly soluble and difficult to precipitate completely.

The compound having the composition $Zr_2O_3(KSO_4)_2,8H_2O$ was obtained by the action of a neutral solution of zirconium sulphate on normal potassium sulphate. This compound has an advantage over the other two compounds in being comparatively easily and completely precipitated. It may be mentioned that the difficulty in completely precipitating the other two compounds is to a large extent due to the presence of free acid in the solutions.

For these reasons our choice was naturally in favour of this last compound for the gravimetric estimation of potassium.

(c) *The Gravimetric Estimation of Potassium.*

In all the experiments in which the estimations of potassium were carried out by the zirconium sulphate method, exactly 10 c. c. of the potassium sulphate solution of varying concentrations were taken

in clean dry beakers. Equal volumes of concentrated solutions of zirconium sulphate were added. The mixture after shaking was allowed to stand at 0° for two or three hours. The precipitate was transferred to a weighed Gooch crucible, washed first with a little cold water, then with a 5% solution of alcohol and finally with ether. It was then dried at 130° to a constant weight. The residue so obtained was analysed and it had the composition represented by the formula, $Zr_2O_3(KSO_4)_2$, from which the percentage of potassium was calculated. The results of a large number of experiments on the estimation of potassium from potassium sulphate solutions along with the results obtained on potassium estimations with the other well-known methods are given in the following table.

TABLE I.

Calc. amt. of potassium in the sample.	Amount of potassium in g. found in the sample.		
	Zirconium sulphate method.	Sodium cobaltinitrite method.	Perchlorate method.*
0·3590 g.	0·3587 g.	0·3589 g.	0·3586 g.
0·3231	0·3228	0·3225	0·3221
0·2872	0·2868	0·2868	0·3869
0·2513	0·2509	0·2512	0·2508
0·2154	0·2145	0·2150	0·2149
0·1795	0·1788	0·1787	0·1789
0·1436	0·1434	0·1431	0·1429
0·1077	0·1072	0·1074	0·1072
0·0718	0·0715	0·0715	0·0712
0·0359	0·0356	0·0357	0·0356
0·0179	0·0178	0·0178	0·0177

(d) *Influence of the Presence of the Ammonium Ions on the Accuracy and Sensitivity of the Zirconium Sulphate Method.*

It is a well-known fact that perchloric acid, chloroplatinic acid and sodium cobaltinitrite methods fail to give satisfactory results when ammonium ions are present. Therefore, experiments were carried out to see if the present method would work in the presence of ammo-

* For the estimation of potassium by perchlorate method, solutions of potassium chloride having the same concentrations of potassium as in the corresponding potassium sulphate solutions were used.

nium ions, or not. For this purpose, 5 c. c. of a 10 per cent. solution of ammonium sulphate were added to 5 c. c. of a potassium sulphate solution and throughly shaken together, then 5 c. c. of a concentrated solution of the zirconium sulphate were added so as to make a total volume of 15 c.c. A number of experiments were carried out in which the concentration of the potassium sulphate solution was varied and that of the other solutions was kept constant. The results of the experiments are scheduled in the following table.

TABLE II.

Zirconium sulphate solution = 5 c. c. of a 20·11 % solution.

Potassium sulphate solution = 5 c. c. of varying strength.

Ammonium sulphate solution = 5 c. c. of a 10 % solution.

Calculated amount of potassium in the sample.	Amount of potassium found in the sample.
0·1077 g.	0·1078 g.
0·0718	0·0716
0·0359	0·0356
0·0179	0·0178
0·0090	0·0088

The results given in the above table quite clearly show that the presence of ammonium ions in no way interferes with the estimation of potassium by the zirconium sulphate method. This is a distinct advantage over the other methods. This conclusion is in agreement with the recent publication of the results and conclusion of Reed and Withrow (*J. Amer. Chem. Soc.*, 1928, **50**, 2985).

(e) *Influence of the Presence of Sodium and Lithium Ions on the Accuracy of the Zirconium Sulphate Method.*

Reed and Withrow (*J. Amer. Chem. Soc.*, 1928, **50**, 1515) have found out qualitatively that the presence of a large amount of sodium sulphate in the potassium sulphate solution retarded the detection of potassium in concentrated sulutions but had very little or no effect when dilute solutions were used. As a result of a large number of preliminary experiments it was found also by us that the time required for the complete precipitation of potassium with zirconium

sulphate went on increasing with the increase in the quantity of sodium sulphate added to the potassium sulphate solution.

Experiments were therefore carried out to find out whether the presence of sodium ions and also that of lithium ions had any influence on the accuracy of the method.

The results of a series of experiments carried out with a view to study the influence of the presence of sodium and lithium ions on the method under investigation are given in the following table: –

TABLE III.

Zirconium sulphate solution = 8 c. c. of 20·11 % solution

Potassium sulphate solution = 2 c. c. of 8 % solution.

Sodium or lithium sulphate solution = 5 c. c. of varying strengths.

Total volume = 15 c. c.

Calculated amount of potassium in each sample = 0·0718 g.

Effect of sodium ions.		*Effect of lithium ions.*	
Amt. of sodium sulphate added.	Potassium experimentally found.	Amt. of lithium sulphate added.	Potassium experimentally found.
0·01 g.	0·0716 g.	0·0105 g.	0·0714 g.
0·02	0·0714	0·0250	0·0713
0·04	0·0718	0·1000	0·0718
0·06	0·0718	0·1000	0·0712
0·08	0·0717	0·2000	0·0716
0·10	0·0713	0·3000	0·0717
0·12	0·0703	0·0000	0·0714
0·14	0·0711	0·5000	0·0714
0·16	0·0714	0·6000	0·0712
0·18	0·0715	0·7000	0·0716
0·20	0·0717	0·8000	0·0715
		0·9000	0·0717
		1·0000	0·0716

Gravimetric Estimation of Rubidium and Caesium.

All the methods which are used for the estimation of potassium are used for the estamition of rubidium and caesium too, since there is a great similarity in the properties of these elements. This close similarity between these elements suggested the idea of the zirconium sulphate method for the estimation of the other two members, beside potassium of the family.

When a neutral solution of zirconium sulphate is added to a saturated solution of rubidium sulphate, a white crystalline precipitate gradually comes down. This precipitate was taken on a weighed filterpaper, washed first with cold water, then with alcohol and finally with ether and dried in a steam oven. The analysis of a number of samples of the compound so prepared showed the composition to correspond to the formula, $Zr_2O_3,(RbSO_4)_2,15H_2O$.

With caesium sulphate and zirconium sulphate, a compound with the composition, $Zr_2O_3(CeSO_4)_2,11H_2O$ is obtained. Thus the double salts obtained by the action of neutral zirconium sulphate on normal rubidium and caesium sulphate are similar to the corresponding potassium salt with the only difference in the number of the molecules of water of crystallisation.

Rubidium and caesium were thus precipitated as double salts by normal zirconium sulphate solution. The method followed in their precipitations and estimationds was exactly the same as described under the "Gravimetric estimation of potassium."

In the following tables, the results of the estimations of rubidium and caesium from their respective sulphate solutions by the zirconium sulphate method have been tabulated.

TABLE IV.

Rubidium.		*Caesium.*	
Calculated amt. of rubidium in the sample.	Amt. of rubidium experimentally found out.	Calculated amt. of caesium in the sample.	Amt. of caesium experimentally found out.
0·1033 g.	0·1030 g.	0·1249 g.	0·1245 g.
0·0930	0·0929	0·1124	0·1120
0·0827	0·0825	0·0999	0·0994
0·0723	0·0721	0·0874	0·0872
0·0620	0·0616	0·0749	0·0745
0·0517	0·0514	0·0624	0·0621
0·0413	0·0411	0·0499	0·0496
0·0310	0·0309	0·0375	0·0373
0·0207	0·0206	0·0250	0·0248
0·0104	00·102	0·0125	0·0122

TABLE V.

Effect of Ammonium Ions.

2 C.c. of rubidium or caesium sulphate solution.

5 C.c. of 20·13% zirconium sulphate solution.

3 C.c. of ammonium sulphate solution of varying strength.

Total volume = 10 c.c.

	Rubidium sulphate.		*Caesium sulphate.*	
Amount of ammonium sulphate in the sample.	Calc. amount of rubidium in the sample.	Amt. of rubidium found experimentally.	Calculated amt. of caesium in the sample.	Amount of caesium found experimentally.
0·0062 g.	0·0413 g.	0·0410 g.	0·0499 g.	0·0497 g.
0·0125	0·0413	0·0411	0·0499	0·0497
0·0250	0·0413	0·0409	0·0499	0·0499
0·0500	0·0413	0·0412	0·0499	0·0498
0·1000	0·0413	0·0410	0·0499	0·0495
0·2000	0·0413	0·0409	0·0499	0·0496
0·3000	0·0413	0·0411	0·0499	0·0496
0·4000	0·0413	0·0412	0·0499	0·0497
0·5000	0·0413	0·0408	0·0499	0·0496
0·6000	0·0413	0·0409	0·0499	0·0499

TABLE VI.

Effect of Sodium Ions.

2 C.c. of rubidium or caesium sulphate solution.

5 C.c. of 20·13% zirconium sulphate solution.

3 C.c. of sodium sulphate solution of varying concentrations.

Total volume = 10 c.c.

	Rubidium sulphate.		*Caesium sulphate.*	
Amt. of sodium sulphate in the sample.	Calc. amt. of rubidium in the sample.	Amt. of rubidium found out experimentally.	Calc. amt. of caesium in the sample.	Amount of caesium found out experimentally
0·0025 g.	0·0413 g.	0·0411 g.	0·0499 g.	0·0496 g.
0·0050	0·0413	0·0408	0·0499	0·0497
0·0100	0·0413	0·0409	0·0499	0·0496
0·0200	0·0413	0·0410	0·0499	0·0495
0·0400	0·0413	0·0411	0·0499	0·0497
0·0600	0·0413	0·0409	0·0499	0·0496
0·0800	0·0413	0·0409	0·0499	0·0498
0·1000	0·0413	0·0410	0·0499	0·0496
0·1200	0·0413	0·0411	0·0499	0·0498

TABLE VII.

Effect of Lithium Ions.

2 C.c. of rubidium or caesium sulphate solution.

5 C.c. of 20·13% zirconium sulphate solution.

3 C.c. of lithium sulphate solution of varying concentrations.

Total volume=10 c.c.

	Rubidium sulphate.		*Caesium sulphate.*	
Amt. of lithium sulphate in the sample.	Calc. amt. of rubidium in the sample.	Amt. of rubidium found out experimentally.	Calc. amt. of caesium in the sample.	Amount of caesium found out experimentally.
0·0003 g.	0·0413 g.	0·0411 g.	0·0499 g.	0·0497 g.
0·0006	0·0413	0·0410	0·0499	0·0496
0·0012	0·0413	0·0412	0·0499	0·0496
0·0025	0·0413	0·0411	0·0499	0·0497
0·0500	0·0413	0·0410	0·0499	0·0495
0·1000	0·0413	0·0412	0·0499	0·0498
0·2000	0·0413	0·0410	0·0499	0·0496
0·4600	0·0413	0·0411	0·0499	0·0497
0·6000	0·0413	0·0411	0·0499	0·0498

Summary.

1. Potassium, rubidium and caesium can be estimated accurately by precipitating them in the form of the double salts with zirconium sulphate provided that such interfering ions as would also react with either zirconium or the sulphate ions to give insoluble precipitates are previously eliminated. The results obtained by this method are as accurate as those obtained by the sodium cobaltinitrite and the perchloric acid methods (*vide* Table I).

2. In order to estimate potassium, rubidium or caesium by this method they should be present in the form of sulphates. This is, however, by no means difficult since almost all the well-known compounds of these elements are easily converted into the corresponding sulphates on treatment with sulphuric acid.

3. This method does not serve satisfactorily in acidic solutions.

4. The presence of ammonium ions in the solutions of the sulphates of either potassium, rubidium or caesium does not in any way interfere with the accuracy of this method. This is a distinct advantage over the sodium cobaltinitrite, the platinum chloride and the perchloric acid method (*vide* Tables II and V).

5. The presence of sodium ions beyond prolonging the time required for complete precipitation in no way interferes with the accurate determination of these elements (*vide* Tables III and VI).

6. The presence of lithium ions, too, has no effect on the accuracy of this method (*vide* Tables III and VII).

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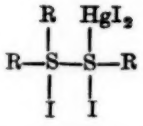
Complexes of Mercuric Iodide with Alkyl Sulphonium Iodides.

By Prafulla Chandra Rây and Nadiabehari Adhikary.

One of us has been investigating the interaction of alkyl iodides on mercury mercaptide nitrites for the last fifteen years (Rây *J. Chem. Soc.*, 1916, **109**, 131, 602; 1917, **111**, 111; 1919, **115**, 216, 541, 548, 1148). It has been shown all along that the products have the empirical formula R_2S_2,HgI_2,RI which are supposed to have the constitution (I).



(I)

(II)

Smiles has, by the interaction of ethyl sulphide and disulphide with ethyl iodide and mercuric iodide, prepared a compound to which he assigns the empirical formula Et_3SI,HgI_2 and the constitutional formula (II), the sulphur functioning as sexavalent (*J. Chem. Soc.*, 1900, **77**, 163; 1907, **91**, 1397). He, however, does not explicitly state that an atom of sulphur is dropped.

Cadmium from its position in the second group of the periodic system was expected to yield a series of analogous compounds of the type (II). This expectation has been realised though in a modified form.* An anomalous behaviour was noticed at the outset.

* This has been found by Mr. S. K. Banerjee working in the laboratory, under Rây's supervision.

On treating both ethyl sulphide and disulphide with the iodide of of the metal and ethyl iodide, it was found that one and the same compound of the formula $[2(Et_3SI)]CdI_2$ was invariably obtained and not even a trace of $[Et_2S_2,CdI_2,EtI]$.

This led the authors to repeat the analogous experiment in the mercury series. In this case two series of compounds were obtained depending upon the method of preparation namely, $[Et_2S, HgI_2,EtI]$ and $[2(Et_2S)HgI_2,2EtI]$. It was thus evident that an atom of sulphur is dropped from ethyl disulphide resulting, at first, in the formation of the monosulphide, which acting upon the ethyl iodide gives rise to *trimethyl sulphonium iodide* which in turn produces the complex $Et_3S.HgI_3$ thus:

$$Et_2S_2 \longrightarrow Et_2S \xrightarrow{EtI} Et_3SI \xrightarrow{HgI_2} Et_3S{\cdot}HgI_3$$

This reaction is in fact strictly comparable to that which takes place in the system potassium iodide and mercuric iodide:

$$KI + HgI_2 \longrightarrow K{\cdot}HgI_3$$

$$2KI + HgI_2 \longrightarrow K_2HgI_4$$

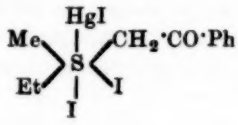
The conductivity measurement of the complex in acetone solution fully confirms this view.

Rây and Kumar (*J. Chem. Soc.*, 1921, **119**, 1643) measured the conductivity of a large series of the so-called type R_2S_2,HgI_2,RI in acetone and found that every member of the group had almost exactly the same conductivity as that of potassium iodide; in other words, there were two monovalent ions present in the solution. No explanation could then be offered as they were then mistakenly taken to be chain-compounds of the sulphonium type (*loc. cit.*).

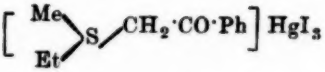
In the light of the present investigation the true explanation has been forthcoming. In these compounds the sulphur is in reality quadrivalent. We are all along dealing with compounds of the type $[Et_3SI,HgI_2]$ or rather $[Et_3S]HgI_3$ and it is but natural that in acetone solution they should have the conductivity of a compound having two monovalent ions.

Hilditch and Smiles (*J. Chem. Soc.*, 1907, **91**, 1306) in grouping all the above radicles round sexavalent sulphur refer to the previous work of Pope and Neville (*J. Chem. Soc.*, 1902, **81**, 1560) on methyl-ethylphenacylthetine and its conversion into the mercuri-iodide

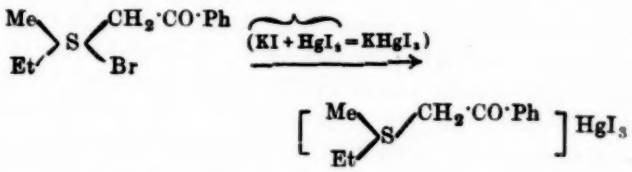
compound as conclusive evidence of the existence of such a sulphur atom. The present authors have recently prepared this identical compound and have found that its conductivity is exactly of the same order as that of Hilditch and Smiles' aforesaid compound, thus:



is in reality

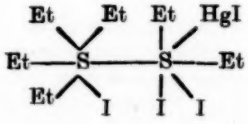


According to the view now put forward, Pope and Neville's reaction may be thus represented: –



the sulphur being quadrivalent. Conductivity measurement fully bears out this view. The fact that the optical activity of the thetines disappears in their mercuri-iodide derivatives may possibly be attributed to racemisation during the complex formation.

Rây repeated Smiles' experiment and corroborated it. It was noticed, however, that a small quantity of another compound was simultaneously produced conforming to the formula, $Et_4S_2,2EtI,HgI_2$ and this was explained by taking both the sulphur atoms as sexavalent, thus:



(*J. Chem. Soc.*, 1919, **115**, 549). This latter formula should now be interpreted as $2Et_3SI,HgI_2$ or rather as $[Et_3S]_2{\cdot}HgI_4$. In fact, this compound is of the same type as K_2HgI_4.

It has been found that if the components, ethyl disulphide and mercuric iodide, be mixed in molecular proportions with an excess of ethyl iodide and the reaction be allowed to go on for ten hours or more on water-bath till a solid mass is produced the main products conform to the latter type. This being almost insoluble in cold acetone or water, its conductivity measurement was not possible. However, its direct production from mercuric iodide and triethylsulphonium iodide leaves no doubt about its constitution.

A comparison of the conductivity tables shows that both the compounds $Et_3S{\cdot}HgI_3$ and $KHgI_3$ dissociate on dilution into mercuric iodide and so the conductivity values rise with dilution in these cases. But in the instance of methylethylphenacylthetine mercuri-iodide such dissociation does not take place and hence the conductivity values are of the order of potassium iodide (*vide* Experimental).

Not only methyl and ethyl disulphides part with an atom of sulphur but methyl and ethyl trisulphides also behave like the corresponding disulphides; in other words, the latter drop off two atoms of sulphur when treated with mercuric iodide and an excess of alkyl iodides.* In fact, the dropping of sulphur atoms in the case of polysulphides is not uncommon in reactions with metallic halides (*cf. J. Chem. Soc.*, 1922, **121**, 1279).†

Experimental.

Methyl Sulphide, Methyl Iodide and Mercuric Iodide.

Three times the calculated quantity of methyl iodide was added to an equimolecular mixture of methyl sulphide and mercuric iodide in acetone in the cold. On shaking, the mercuric iodide gradually went into solution and a light yellow crystalline substance separated out. The reaction was completed in an hour.

* The preparation of methyl and ethyl trisulphides in quantity, as well as in a state of purity, will form the subject of a future communication.

† The estimation of sulphur by Carius' method followed by fusion with Na_2CO_3 and KNO_3 often gives divergent values. Hence the composition of the compounds had to be determined from the estimations of mercury, iodine and carbon. The molecular weight being often as high as 732, the formulæ with one or more sulphur atoms could be accommodated with almost equal ease to the analytical data. Hence the phenomenon of dropping off of sulphur evidently escaped notice in earlier investigations.

The precipitate was filtered off and recrystallised from acetone; m.p. 163°. (Found: Hg, 30·27; I, 57·63; C, 5·49. $C_3H_9I_3SHg$ requires Hg, 30·39; I, 57·90; C, 5·47 per cent.).

Trimethyl Sulphonium Iodide and Mercuric Iodide.

When equimolecular proportions of trimethylsulphonium iodide in water and mercuric iodide in acetone were mixed, a pale yellow crystalline substance gradually separated out. The reaction was completed in half an hour. The crystals after purification by recrystallisation from acetone melted at 163°. (Found: Hg, 30·01 per cent.).

Dimethyl Sulphide, Methyl Iodide and Mercuric Iodide.

When equimolecular proportions of dimethylsulphide and mercuric iodide were heated on a water-bath for an hour with an excess of methyl iodide, a tarry mass separated out. The supernatant brown liquid, mostly methyl iodide, was decanted off, and the black mass was dissolved in acetone. On the addition of ether a yellow crystalline mass was obtained. This was then redissolved in acetone and precipitated again with ether. Finally it was crystallised from acetone; m.p. 163°. The identity of the products of three distinct methods of preparation is thus established.

Dimethyl Trisulphide, Methyl Iodide and Mercuric Iodide.

Equimolecular proportions of dimethyl trisulphide and mercuric iodide were digested with excess of methyl iodide on water-bath for 2 to 3 hours, when the whole mass became tarry. The brown supernatant liquid was drained off and the black solid mass treated with minimum quantity of acetone when the adhering tar first went into solution leaving behind a yellow crystalline mass which gradually dissolved on refluxing on water-bath. When ether was added to the acetone solution, a light yellow precipitate was obtained. This was twice dissolved in acetone and precipitated with ether and finally crystallised from acetone, m.p. 189°. (Found: Hg, 22·92; C, 8·03. $C_6H_{18}I_4S_2Hg$ requires Hg, 23·26; C, 8·35 per cent.).

The above compound was directly obtained when trimethylsulphonium iodide and mercuric iodide were mixed in proportions of 2 mols.: 1 mol. in a mixture of acetone and water. The yellow solution on evaporation of acetone yielded a light yellow crystalline mass which after purification by recrystallisation from acetone melted at 189°. (Found: Hg, 22·99 per cent.).

Dimethyl Disulphide, Methyl Iodide and Mercuric Iodide.

The method of preparation was the same as in the previous case with dimethyltrisulphide but in this instance the proportions of dimethyldisulphide and mercuric iodide should be as 2 : 1. The light yellow crystals after purification melted at 189°.

Ethyl Sulphide, Ethyl Iodide and Mercuric Iodide.

The method of preparation was the same as in the corresponding methyl series. Bright yellow crystals were obtained which melted at 110°. (Found: Hg, 28·03; C, 10·41. $C_6H_{15}I_3SHg$ requires Hg, 28·57; C, 10·28 per cent.).

Diethyl Disulphide, Ethyl Iodide and Mercuric Iodide.

The method of preparation was the same as in the case of methyl disulphide, methyl iodide and mercuric iodide, but the mixture in this case was heated on water-bath for 3 hours and two compounds were simultaneously formed, *viz.*, $Et_3S{\cdot}HgI_3$, which being very soluble in cold acetone was separated from the compound $[Et_3S]_2{\cdot}HgI_4$, which was moderately soluble in hot but almost insoluble in cold acetone. After recrystallisation, the former melted at 110°, and the latter at 148°. In order to get a greater yield of the compound melting at 148°, the reaction should be allowed to proceed for ten hours or more. (Found: Hg, 28·12. $C_6H_{15}I_3SHg$ requires Hg, 28·57 per cent.).

The compound $Et_3S{\cdot}HgI_3$ may be obtained directly from an equimolecular mixture of triethylsulphonium iodide and mercuric iodide in a mixture of acetone and water. After recrystallisation from acetone the compound melted at 110°.

The identity of the compound by the three distinct methods of preparation is thus proved.

Molecular Conductivities in Acetone at 25·6°.

$Et_3S{\cdot}HgI_3$.		$KHgI_3$.	
Molar conc.	Molar conductivity.	Molar conc.	Molar conductivity.
0·00196	145·1	0·0018	131·0
0·00098	155·1	0·0009	152·1
0·00049	164·9	0·00045	159·2
0·000245	174·1	0·000225	174·7

Diethyl Trisulphide, Ethyl Iodide and Mercuric Iodide.

The method of preparation was the same as in the corresponding methyl series. The product being insoluble in cold acetone, was recrystallised from boiling acetone, as light yellow crystals, m.p. 148°. (Found: Hg, 21·06; I, 52·69; C,15·09. $C_{12}H_{30}I_4S_2Hg$ requires Hg, 21·14; I, 53·70; C, 15·22 per cent.).

The above compound was also directly prepared from triethylsulphonium iodide and mercuric iodide when they were mixed in proportions of 2:1 in a mixture of acetone and water. A light yellow crystalline mass separated out which on recrystallisation from hot acetone, melted at 148°. (Found: Hg, 20·91; C, 15·47. $C_{12}H_{30}I_4S_2Hg$ requires Hg, 21·14; C, 15·22 per cent.).

Methylethylphenacylthetine Mercuri-Iodide.

This compound was obtained by the method of Pope and Neville and after purification melted at 129°. (Found: C, 17·27. $C_{11}H_{15}OI_3SHg$ requires C, 16·99 per cent.).

Molecular Conductivity in Acetone at 18·4°.

Molar conc.	Molar conductivity.
0·00178	88·6
0·00089	95·7
0·000445	101·1
0·0002225	106·0
0·00011125	114·8

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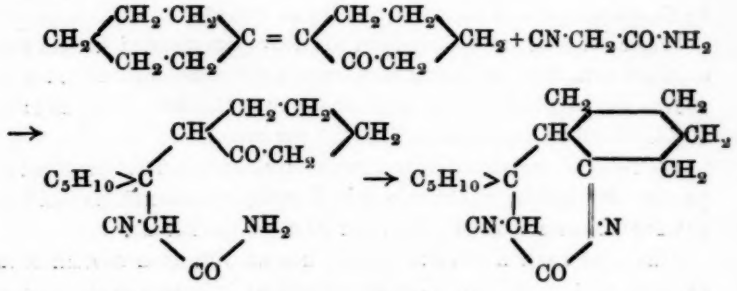
Form tion of Heterocyclic Compounds. Part V. Condensation of *cyclo*Hexylidene*cyclo*hexanone with Cyanoacetamide.

By Hemendra Kumar Sen and Nirmal Chandra Neogi.

As hexahydro-2-quinolone synthesised by one of us (Sen, *J. Chem. Soc.*, 1915, **107**, 1351) has been found to be a powerful bactericide, further synthesis of analogous quinoline derivatives seemed to be of more than ordinary synthetic interest. The *cyclo*hexylidene*cyclo*hexanones appeared to provide a class of suitable starting material for this purpose, as the conjugated double-bonded system in these compounds offers an easy means of synthesising quinolone, by condensing them with cyanoacetamide in the presence of sodium ethoxide or piperidine (*loc. cit.*). A further extension of such condensation may be made with hydroxymethyleneketones derived from these *cyclo*hexylidene*cyclo*hexanones, which do not appear to have been prepared and investigated before. The therapeutic value of these compounds is now under investigation, whilst below is given a description of the experimental work performed in this connection. The quinolone derivatives were formed according to the following scheme:



Experimental.

Condensation of cyclo*Hexylidene*cyclo*hexanone with Cyanoacetamide in the Presence of Sodium Ethoxide.*—Dry hydrogen chloride was passed into *cyclo*-hexanone (50 g.) at 0°. After leaving overnight the hydrogen chloride was expelled by heating on the sand-bath and the residual liquid subjected to vacuum distillation. The

fraction collecting at 150-153°/20 mm. was pure *cyclo*hexylidene-*cyclo*hexanone (26 g.), identified by its oxime and semicarbazone. The solid compound with hydrogen chloride described by Wallace (*Ber.*, 1907, **40**, 70) could not be isolated.

Metallic sodium (0·52 g.) dissolved in absolute alcohol was added to a solution of cyanoacetamide (1·9 g.) dissolved in absolute alcohol. To the mixture so obtained, *cyclo*hexylidene*cyclo*hexanone (4 g.) dissolved also in absolute alcohol was gradually added with occasional shaking, and the whole kept overnight. Next day, carbon dioxide was passed into the mixture, and the solid that separated out was filtered and washed with absolute alcohol. The *solid product* was boiled with water when a white residue (1 g.) was left behind. It crystallised from acetic acid, m.p. 340-341°. (Found: N, 11·19. $C_{15}H_{20}ON_2$ requires N, 11·47 per cent.).

Hydrolysis of the product with fuming hydrochloric acid or 80% sulphuric acid gave either the unchanged substance or decomposition products from which no crystalline pure compound could be isolated.

4'-Methyl-cyclo*hexylidene*-*4-methyl*-cyclo*hexanone* was prepared by passing dry hydrogen chloride into 4-methyl *cyclo*-hexanone as usual. It boils at 170-172°/5 mm. Yield, 26 g. of the purified product from 46 g. of the ketone. The compound was previously prepared by Marcel Godehot and Fedox Taboury (*Compt. rend.*, 1919, **169**, 1168) by passing the vapour of 4-methyl*cyclo*hexanone over heated calcium oxide. The identity of the two was established by the preparation of an oxime melting at 153-154°.

The condensation product from the above unsaturated ketone and cyanoacetamide in the presence of sodium ethoxide was obtained as above and crystallised from alcohol, m.p. 285-287°. (Found: N, 10·43. $C_{17}H_{24}ON_2$ requires N, 10·29 per cent.).

3'-Methyl-3-cyclo*hexylidene*-*3-methyl*cyclo*hexane-6-one* prepared by passing dry hydrogen chloride into 3-methyl*cyclo*hexanone boils at 165-166°/20 mm. Yield 30 g. from 50 g. of the ketone.

The condensation product of this ketone with cyanoacetamide in the presence of sodium ethoxide, isolated as indicated in the case of the other isomer, crystallised from acetic acid, melting at 326-328°. (Found: N, 10·18. $C_{17}H_{24}ON_2$ requires N, 10·29 per cent.).

*Condensation of Hydroxymethylene*cyclo*hexylidene*cyclo*hexanone with Cyanoacetamide in the Presence of Piperidine.*

Hydroxymethylene cyclo-*hexylidene*cyclo*hexanone.*—*cyclo*-Hexylidene*cyclo*hexanone (18 g.) was mixed with amyl formate

(11 g.) and dry ether (100 c.c.). Metallic sodium (2·2 g.) in the form of wire was then added to the solution slowly with frequent disintegration of the incrustation on the sodium by means of a stout glass rod. The mixture was kept in ice during the experiment and allowed to stand overnight. The sodium salt of the hydroxymethylene derivative which separated out, was dissolved in water and the solution separated from the ethereal layer containing the unacted formate and *cyclo*hexylidene*cyclo*hexanone as also some amyl alcohol. The aqueous solution was extracted with some more ether, and then acidified with dilute acetic acid in the cold when an oil separated. The oil was extracted with ether, dried over ignited sodium sulphate and distilled in vacuum. The liquid (7 g.) distilled at 170-172°/15 mm. It gave a violet coloration with alcoholic ferric chloride. (Found: C, 75·24; H, 8·98. $C_{13}H_{18}O_2$ requires C, 75·73; H, 8·73 per cent.).

The *copper* salt was formed when the hydroxymethylene compound was digested with a saturated solution of copper acetate for 4 hours on the water-bath. A solid separated which when crystallised from absolute alcohol melted at 174-175°. (Found: Cu, 13·27. $C_{26}H_{34}O_4Cu$ requires Cu, 13·1 per cent.).

The *pyrasole* derivative prepared by the action of semicarbazide hydrochloride in the presence of fused sodium acetate in glacial acetic acid, melted at 258° after crystallisation from acetic acid. The product dissolved in dilute hydrochloric acid and was regenerated by alkali. It is sparingly soluble in almost all organic solvents. (Found: N, 13·76. $C_{13}H_{18}N_2$ requires N, 13·86 per cent.).

The condensation of the hydroxymethylene compound with cyanoacetamide was brought in the usual way (*cf.* Sen, *loc. cit.*). Crystals began to separate after one hour, but the reaction mixture was allowed to stand overnight. Crystallised twice from acetic acid using animal charcoal, the substance melted at 230-232°. The product was insoluble in water, dissolved in caustic soda, and exhibited violet fluorescence in alcohol and acetic acid solutions. It absorbed bromine, indicating the presence of the double bond at the *cyclo*hexylidene junction. (Found: C, 75·18; H, 7·27; N, 11·43. $C_{16}H_{18}ON_2$ requires C, 75·59; H, 7·08; N, 11·02 per cent.).

Hydroxymethylene-4 - *methyl*(4′-*methyl*cyclo*hexylidene*) - 6-cyclo*hexanone* prepared as above boiled at 180°/11 mm. Yield 7 g. from 20 g. of the ketone. (Found: C, 77·0; H, 9·29. $C_{15}H_{22}O_2$ requires C, 76·92; H, 9·4 per cent.).

The *pyrazole* derivative prepared as usual melted at 262-263°. It dissolved in dilute hydrochloric acid and was sparingly soluble inalmost all organic solvents. (Found: N, 12·03. $C_{15}H_{22}N_2$ requires N, 12·17 per cent.).

The condensation product with cyanoacetamide obtained as usual, crystallised from acetic acid in plates, m. p. 243-244°. It absorbed bromine, dissolved in caustic soda and exhibited fluorescence in alcoholic solution. (Found: N, 10·17 $C_{18}H_{22}ON_2$ requires N, 9·93 per cent.).

Condensation of Acetyl cyclo*hexylidene*cyclo*hexanone with Cyanoacetamide.*—Acetyl *cyclo*hexylidene*cyclo*hexanone was prepared in the usual way by condensing *cyclo*hexylidene *cyclo*hexanone (25 g.) with ethyl acetate (80 g.) and metallic sodium (3·25 g.). The fraction distilling at 170-180°/20 mm. was redistilled when a liquid (10 g.) boiling at 170-175°/20 mm. was obtained. The liquid was not pure, and no definite copper salt could be isolated, It gave a violet coloration with alcoholic ferric chloride, characteristic of β-diketones. But an oxime could be separated melting at 145-147° which corresponded to that of *cyclo*hexylidene *cyclo*hexanone. It seemed, therefore, that the liquid was a mixture of *cyclo*hexylidene*cyclo*hexanone and acetyl *cyclo*hexylidene *cyclo*hexanane. On condensing, however, the impure liquid with cyanoacetamide in the presence of piperidine in the usual way a product melting at 245-246° was obtained which absorbs bromine. The condensation conducted in the presence of sodium ethoxide and absolute alcohol gave rise to two products. Into the condensation mixture, carbon dioxide was passed and the total solid thus separated, was boiled with absolute alcohol and filtered. From the filtrate a solid could be separated which when crystallised from alcohol melted at 245-246° and was identical with the product obtained when the condensation was effected in the presence of piperidine. The residue on the filter was next boiled with water when a white residue was left behind. Crystallising from acetic acid, it melted at 340-341° and was identical with the product obtained by condensing *cyclo*hexylidene *cyclo*hexanone with cyanoacetamide. It did not absorb bromine as expected. (Found: N, 10·64. $C_{17}H_{20}ON_2$ requires N, 10·45 per cent.).

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Examination of the Unsaturated Acids in Fish Oil.

Part I. Oil of Labeo Rohita.

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While engaged in investigating the possibilities of deodourising fish oils without having recourse to the well-known process of hydrogenation, the authors had occasion to refer to the literature on the nature of the unsaturated acids likely to be present and were surprised to find that there were no data available as to the nature of acids in tropical fish oils with which they were working while the acids present in some fish oils of colder climates were only imperfectly known. Efforts were therefore directed to the examination of the unsaturated acids occurring in the stomach-oil of *Labeo Rohita* (the "ruhu" of Indian rivers), which is extensively used for edible purposes.

This lack of information regarding the chemical nature of fish oils is no doubt due to the great experimental difficulties attending the investigation of marine oils. Owing to the unsaturation of the fatty acids and the consequent possibilities of a large number of isomerides as well as the complexity of the mixture of fatty acids of similar nature occurring in fish oils, the difficulty of experimental investigation is greatly multiplied.[1]

Hofstaedter (*Annalen*, 1854, **91**, 177) was the first to point out the presence of unsaturated acids in marine oils. The most notable workers in recent years are Fahrion, (*Chem. Ztg.*, 1893, **17**, 521, 684), Bull (*Ber.*, 1906, **39**, 3570), Tolman (*Ind. Eng. Chem.*, 1909, **1**, 341), Twitchell (*ibid*, 1914, **6**, 564; 1917, **9**, 581), Tsujimoto (*J. Coll. Eng. Imp. Uni. Tokyo*, 1906, **4**, 1; *J. Chem. Ind. Japan*, 1926, **23**, 1007), Brown and Beal (*J. Amer. Chem. Soc.*, 1923, **45**, 1289), Armstrong and Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 180T) and Hilditch and Lovern (*ibid*, 1928, **47**, 105T) who investigated the following marine oils:—cod-liver, menhaden, sardine,

[1] The difficulties of isolating the unsaturated acids in the pure state may be appreciated from the fact that even a simple unsaturated acid such as oleic acid, has been obtained in pure condition only recently (Holde and Gorgas, *Z. angew. Chem.*, 1926, **39**, 1443).

herring, salmon, and lofoten oils—all obtained from colder climates. It has been found by these authors that chemically these marine oils are similar amongst themselves but quite different from vegetable and animal oils, and contain highly unsaturated acids of high molecular weight containing fourteen to twenty-two atoms of carbon and a maximum of six double bonds in the molecule. Tsujimoto (*loc. cit.*) found an acid of C_{18}-series with four double bonds as an invariable constituent of all fish oils. This acid, named clupanodonic acid, was according to him, responsible for fishy odour. Later however, he found that the acid was really one of C_{22}-series with five double bonds, and transferred the name clupanodonic acid to this compound to indicate the invariable constituent of all fish oils. Some workers have, however, retained the name for the original C_{18}-acid, with the result that a great confusion prevails as to nomenclature. It is interesting to note that in the oil under investigation, the authors could not detect either the C_{18}- or C_{22}-acid.

The fish oil under investigation was extracted in the laboratory from fresh samples and was found to be free from any nitrogenous matter. It was light yellow in colour, and when preserved in well-stoppered bottles, did not turn rancid for months; though on exposure to air it turned reddish and developed a more objectionable odour. On standing, a solid matter, the so-called fish stearin, separated out. This fish stearin is evidently less unsaturated than the liquid oil, the iodine value of the former being 121·4 (Wijs) and of the latter 137·35, while that of the average oil is 130·6. The usual constants of the oil are given below:—

Specific gravity at 15°	... 0·9230.
Refractive index	... 1·4622 at 29°.
Optical activity	... Nil.
Saponification value	... 191·4
Acid value	... 1·116
Hehner value	... 91·1
Reichert-Meissel value	... 0·668
Unsaponifiable matter	... 0·34%
Acetyl value	... Nil.
Iodine value (Wijs)	
Oil from smaller fish	... 61·65
,, ,, bigger ,,	... 118·65
,, ,, biggest ,,	... 130·60
Glycerol	... 10·2%
Loss of volatile matter at 200°, for 2 hrs.	... 1·63%

It will be observed that the iodine value of the oil changes to an enormous extent according to the state of development of the fish, the older and bigger fish yielding oils of higher iodine value. This has also been observed by other investigators in the case of linseed oil—the oil from the ripe seed being more unsaturated than those from the raw. The nature of fish oils is also dependent on climatic conditions—those from colder climates being less saturated than tropical oils (*J. Soc. Chem. Ind.*, 1925, **44**, 182T).

The oil from the largest fish having $I.V_a$ (Iodine value) 130·6 was used for the purpose of this investigation. The mixed fatty acids obtained from this oil by usual methods had the following characteristics.

Melting point	..	39°
Titer (solidifying point)	...	29°
Iodine value	...	149·6
Mean M.W.	...	295·3

The mixed acids had the characteristic odour of fish oil. They were separated into solid and liquid acids for the purpose of examination.

Of the different methods of separating saturated from unsaturated acids, the authors have found the lead-salt-alcohol method of Twitchell (*Ind. Eng. Chem.*, 1921, **13**, 806) the best.[1] While Varrentrapp's lead-salt-ether method gave 38·4% of solid acids, (I.V. 16·3) and 61·6 % of liquid acids (I.V. 170·8), Twitchell's method gave 28·1% of solid acids (I.V. 2·4), and 71·9 % of liquid acids (I.V. 180·8). The liquid acids separated by either method had, unlike the solid acids, the characteristic fishy odour. The liquid acids obtained by Twitchell's process were however, more viscous, due apparently to the absence of any solid acids dissolved in it. This is also in agreement with the high iodine value.

As both the methods of Varrentrapp and Twitchell are extremely laborious and require large amounts of solvents, the authors

[1] No satisfactory separation was possible by barium-soap-benzene method of Farnsteiner (*Z. Nahr. Genussm.*, 1898, (2) **1**, 390) which was used by Brown and Beal in their study of fish oils, part of the solid and oleic acids coming over in the liquid fraction. The recent method of Bertram (*Z. Unters. Lebensmittel*, 1927, **54**, 431), though said to be satisfactory in the case of solid acids is however inapplicable for the separation of liquid acids.

subsequently had recourse to the method of Tortelli and Ruggeri (Lewkowitsch, "Chemical Technology of Oils, Fats and Waxes," 6th Ed., Vol. I, p. 560) which was found to be very suitable to handle large amounts of acid mixtures, though the process could not be used for quantitative purpose. Having separated the unsaturated acids, the authors next proceeded to isolate and identify the various individual acids and to estimate them wherever possible.

Attempts to isolate oleic or any other unsaturated acids by the fractional crystallization of lithium salts (*J. Soc. Chem. Ind.*, 1928, **47**, 30T.) from acetone, or alcohol of different strengths, proved unsuccessful. The acid isolated by this process from the alcohol insoluble lithium salts had I.V., 128·5 and a mean mol. wt. 271·5. This is evidently a mixture of oleic acid with more unsaturated acids of lower molecular weight, perhaps with hexadecatrienoic acid, $C_{16}H_{26}O_2$ found later in these investigations. Attempts to separate the individual acids by fractional distillation of methyl esters in vacuum (5 mm.) were found to be unsatisfactory.

Better results have been obtained by the bromination method. The liquid acids obtained by Tortelli and Ruggeri method (*loc. cit.*) were brominated (1) in 3% ethereal solution in presence of 2 c.c. of glacial acetic acid per gm. of liquid acid at 5° (Lewkowitsch, "Chemical Technology of Oils Fats and Waxes" Vol. I, p. 581): and (2) in 10% dry ethereal solution at −10° without the addition of acetic acid (Eibner and Muggenthaler, *Farben-Zeitung*, 1912, No. 3 ff.). The yield of ether insoluble polybromides by the former method was 23·8% (blackening point 238°-39°) and by the latter method 31·45% (blackening point 237°−38°). Bromination by the latter method is therefore more complete and is in agreement with the observation of Eibner and Muggenthaler, that the more glacial acetic acid used, the lower the yield of hexabromide.

The bromides of the unsaturated fatty acids thus obtained in two fractions (ether soluble and ether insoluble). were examined separately. The ether-insoluble fraction obtained by the second process was an amorphous milky white substance, which became brown on drying at 100°. It had 65·5% bromine.

The usual method of separating the higher polybromides (*e.g.*, of clupanodonic acid) from the lower hexabromides is fractional treatment with benzene. (Lewkowitsch. "Chemical Technology of Oils, Fats and Waxes, Vol. I, p. 584). But in this case a separation by

this method was not possible as both higher and lower bromides were partly soluble in boiling benzene. The desired separation was however effected by chloroform. By repeated treatment of the polybromides with chloroform in the cold, a residue (A) was obtained in sufficiently pure state (blackening point 242°), while the chloroform soluble portion, after distilling off the solvent was again separated into two fractions by treatment with benzene in the cold. The portion insoluble in the cold benzene (B), and purified by treatment with boiling benzene, melted at 171° and was identified as the hexabromide of linolenic acid, while the portion soluble in benzene (C), was found on analysis to have the formula, $C_{17}H_{26}O_2Br_6$ (hexabromide of hexadecatrienoic acid).

Tetrosapentenoic Acid, $C_{24}H_{38}O_2$.—The chloroform insoluble residue (A) was found on analysis to agree with the formula $C_{24}H_{38}O_2Br_{10}$ indicating the existence of an acid of C_{24}-series with five double bonds. (Found: Br, 69·055; C, 24·76; H, 3·37. $C_{24}H_{38}O_2Br_{10}$ requires Br, 69·1; C, 24·87; H, 3·28 per cent.). The only experimental evidence of this acid is found in the work of Carter (*J. Soc. Chem. Ind.*, 1929, **47**, 31T) who found it in mutton-bird oil and identified it through the bromo-compound. From a reference to the original work of Carter it cannot be discovered, how this highly complex bromide, mixed perhaps with other polybromides of highly unsaturated acids, was purified. It is however significant that he found the blackening point of the polybromide to be 200°, while that of our product was 242° (sharp). This is perhaps due to the care with which we purified our bromo-compound with the help of chloroform. It will be observed that the blackening point of octabromostearic acid, $C_{18}H_{28}O_2Br_8$ is 200°, and that the blackening point increases with increase in the number of carbon atoms and in bromine content of the molecule (Lewkowitsch, *loc. cit.*, p. 580). The low blackening point found by Carter may be due either to impurities or to an acid isomeric with our product. Carter has not given any name to this acid. Following the usual scientific nomenclature, the authors prefer to call this 'tetrosapentenoic acid," to indicate twenty-four atoms of carbon with five double bonds, in the molecule.

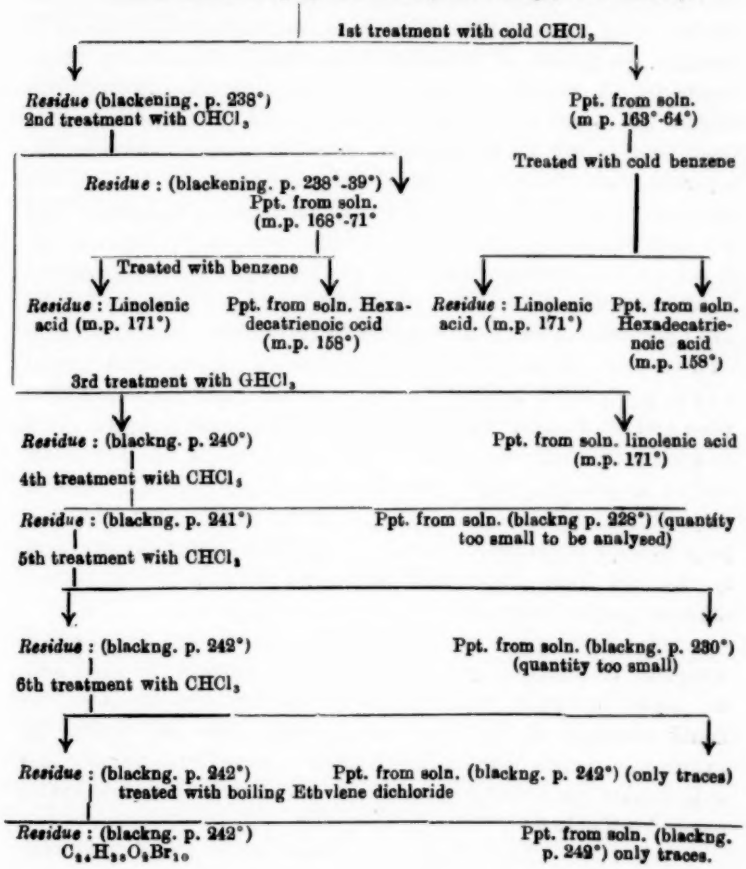
Linolenic Acid. $C_{18}H_{30}O_2$.—Another highly unsaturated acid, $C_{18}H_{30}O_2$, has been found in the mixture of liquid acids. The hexabromide of linolenic acid is generally soluble in benzene. But the hexabromide of linolenic acid as obtained from this fish oil is

evidently insoluble in cold benzene, for the authors have been able to separate the chloroform soluble bromide into two fractions one of which is insoluble in benzene as already stated. The benzene insoluble fraction carefully purified with boiling benzene had m.p. 171° (sharp). The analytical data are in close agreement with formula, $C_{18}H_{30}O_2Br_6$. (Found Br, 63·36 ; C, 28·38 ; H, 4·00 $C_{18}H_{30}O_2Br_6$ requires Br, 63·32; C, 28·49; H, 3·95 per cent.). The melting point of hexabromide of linolenic acid ranges from 185° to 135°, the usual value being 180° (Lewkowitsch, *loc. cit.* p. 584). The difference in m.p. of our product may be accounted for by the large number of possible isomerides of linolenic acid.

It is note-worthy that a considerable amount of hexabromide (m.p. 171°) was isolated from the ether soluble bromides as alcohol insoluble compound. The hexabromide of linolenic acid is apparently soluble in ether, or in the liquid bromides to some extent. On examination of the liquid bromides, the bromine content was found to be too high for dibromostearic acid, apparently due to the solubility of higher bromides. After several unsuccessful attempts to separate the higher bromides from the mixture of liquid bromides (ether soluble), the authors at last found in alcohol a suitable solvent for the lower bromides, a solid hexabromide remaining behind as an insoluble compound. It was purified by recrystallising from alcohol. On analysis this was found to be the hexabromide of linolenic acid, identical with that obtained from the ether insoluble fraction (m.p. 171°, Br., 63·4 per cent.).

Hexadecatrienoic Acid, $C_{16}H_{26}O_2$.—This acid has been definitely identified by the authors in the benzene-soluble fraction (C) obtained from solid polybromides. It melted at 158°, after recrystallisation from benzene. (Found: Br, 65·58; C, 26·11; H, 3·80. $C_{16}H_{26}O_2Br_6$ requires Br, 65·75 ; C, 26·30; H, 3·56 per cent.). A mention of the name of this acid is made by Brown and Beal (*loc. cit.*), who surmised the probable existence of this acid in menhaden oil. The acid in question or any of its derivatives have not been isolated. It is merely surmised that the fraction may be a mixture of 2 parts of clupanodonic acid and one part of hexadecatrienoic acid. It is however obvious that the I. V. and mean mol. wt. of the fraction may be due to the combination of other acids as well. The presence of the hexadecatrienoic acid in the oil of *Labeo rohita* has been proved by the authors by isolation of the pure bromide and its complete analysis.

The scheme of analysis of the solid polybromides as adopted by the authors is shown graphically as follows:


Ether insoluble polybromides (blackening p. 237°-238°),
1st treatment with cold CHCl3
Residue (blackening. p. 238°)
2nd treatment with CHCl3
Ppt. from soln.
(m p. 163°-64°)
Treated with cold benzene
Residue : (blackening. p. 238°-39°)
Ppt. from soln.
(m.p. 168°-71°
Treated with benzene
Residue : Linolenic acid (m.p. 171°)
Ppt. from soln. Hexadecatrienoic ocid (m.p. 158°)
Residue : Linolenic acid. (m.p. 171°)
Ppt. from soln. Hexadecatrienoic acid (m.p. 158°)
3rd treatment with GHCl3
Residue : (blackng. p. 240°)
Ppt. from soln. linolenic acid (m.p. 171°)
4th treatment with CHCl3
Residue : (blackng. p. 241°)
Ppt. from soln. (blackng p. 228°) (quantity too small to be analysed)
5th treatment with CHCl3
Residue : (blackng. p. 242°)
Ppt. from soln. (blackng. p. 230°) (quantity too small)
6th treatment with CHCl3
Residue : (blackng. p. 242°)
Ppt. from soln. (blackng. p. 242°) (only traces)
treated with boiling Ethylene dichloride
Residue : (blackng. p. 242°)
C24H38O2Br10
Ppt. from soln. (blackng. p. 249°) only traces.

Linolic Acid, $C_{18}H_{32}O_2$.—When the ether-soluble bromides, after complete removal of ether, were treated with low-boiling petroleum ether in the usual manner, no separation of any tetrabromide took place, nothing going in solution in boiling petrol. This fact indicates that linolic acid $C_{18}H_{32}O_2$ is not present in any appreciable quantity in the oil under investigation. This conclusion is further supported by the results obtained by the careful oxidation of the

liquid fatty acids with alkaline potassium permanganate in the cold, no tetrahydroxystearic acid (sativic acid) being obtained.

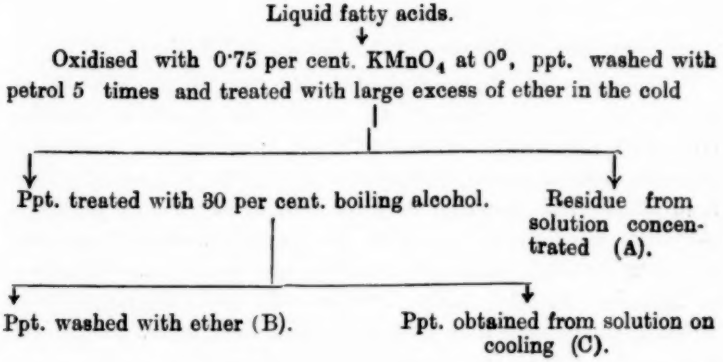
Liquid Bromides.—The filtrate obtained after removal of the insoluble polybromides, consisting of ether-soluble bromides, was washed with aqueous sodium thiosulphate to remove the excess of bromine. A portion of the ether was distilled off and the rest kept overnight. A precipitate, m. p. 168°, was obtained, and on examination was found to be hexabromostearic acid (obtained from linolenic acid). All the higher solid bromides could not, however, be separated with the help of ether. This could be effected by the addition of absolute alcohol when a solid bromide separated (12·5 per cent. of the liquid fatty acids), which as already mentioned was found to be hexabromostearic acid. The liquid bromides obtained from the alcoholic solution is a thick brown syrupy liquid (yield, 145·1 per cent. of the total unsaturated fatty acids, corresponding to 84·0 per cent. bromine free liquid fatty acids). Its bromine content (44·24 per cent.) is too high for dibromostearic acid (obtained from oleic acid). Further separation of the liquid bromides by means of solvents proved unsuccessful. On debrominating the liquid bromides and on brominating them again a very small yield of ether insoluble polybromides was obtained. This blackened at 237°-238°, possessed properties quite similar to the ether insoluble polybromides previously obtained from unsaturated acids and proved to be a mixture of different polybromides.

This shows that a part of the highly unsaturated acids escaped complete bromination and in this form was found in the ether soluble liquid bromides, thus increasing the bromine content of the liquid bromides of less unsaturated acids. This fact makes the quantitative figures of the different acids as stated subsequently only approximate ones those present in the liquid bromides having escaped estimation.

Oxidation of the Liquid Fatty Acids.—The liquid fatty acids obtained by Tortelli and Ruggeri's method were neutralised with potassium hydroxide and oxidised with alkaline potassium permanganate solution (1·5 per cent.) at 28°. The yield of hydroxy-acids obtained by this method was however very poor, and the accompanying unoxidised fatty acids could not be completely removed even by repeated washing with petrol, in which the hydroxy-acids are insoluble. The hydroxy-acids could not thus be obtained in a pure form for analysis.

The mother-liquor (from the permanganate oxidation) obtained after removal of the insoluble hydroxy-acids, was examined for the hydroxy-acids from higher unsaturated acids, (*e.g.*, sativic and linusic acids) but no trace of either could be found. Evidently the higher unsaturated acids were broken down during oxidation.

In order to make the process of oxidation less drastic the liquid fatty acids were next oxidised with a mere dilute solution of potassium permanganate (0·75 per cent.) at 0° (Holde, " Hydrocarbon Oils and Saponifiable Fats aad Waxes, 2nd. English Ed., p. 375). The procedure is represented graphically below.


Liquid fatty acids.
Oxidised with 0·75 per cent. $KMnO_4$ at 0°, ppt. washed with petrol 5 times and treated with large excess of ether in the cold
Ppt. treated with 30 per cent. boiling alcohol.
Residue from solution concentrated (A).
Ppt. washed with ether (B).
Ppt. obtained from solution on cooling (C).

Fraction (A) was recrystallised twice from 95 per cent, alcohol when a milky white stuff was obtained, m. p. 116°-116·5°. The analytical data agree with those for dihydroxyasellinic acid $C_{17}H_{34}O_4$. (Found: Neutralisation value, 185·1; C, 67·17; H. 11·11. $C_{17}H_{34}O_4$ requires neutralisation value, 185·6; C, 67·48; H, 11·33 per cent.) This compound confirms the presence of "asellinic acid" (Fahrions' acid) $C_{17}H_{32}O_2$ in the liquid fatty acids.

The above named acid was discovered by Fahrion (*Chem. Review*, 1926, **3**, 425) in cod-liver oil; the existence of this acid which has an odd number carbon atoms has been doubted by many investigators, notably by Lewkowitsch (*loc. cit.*, Vol. 1, p. 115). Fahrion has however, maintained the existence of this acid in fish oil in a subsequent contribution (*Chem. Umschu.*, 1927, **24**, 6). In view of these contradictory opinions the authors made special efforts to obtain it in the purest possible state and the results confirm Fahrion's observations.

Fraction (B) was also recrystallised several times from 95 per cent. alcohol and was found to melt finally at 125°-26°. The following analytical data identify it as dihydroxystearic acid. (Found: neutralisation value, 176·9; C, 67·87; H, 11·33. $C_{18}H_{36}O_4$ requires neutralisation value 177·5; C, 68·31; H, 11·47 per cent.) The presence of oleic acid in fish oil is thus confirmed.

The usual m. p. of dihydroxystearic acid is stated to be 137°. Other melting points ranging from 137°-119° (Lewkowitsch. *loc. cit.*, Vol. I, 233.) are also found in literature. The m. p. of the dihydroxystearic acid obtained from whale oil by Armstrong and Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 182T) is 124°-25° which is in close agreement with ours.

Approximate Estimation of the Unsaturated Acids.

Estimation of Tetrosapentenoic acid, $C_{24}H_{32}O_2$ 100 G. of liquid fatty acids gave 31·45 g. of ether-insoluble bromides (Br, 55·5 per cent.). Thus 10·75 per cent. of the liquid acids gave the ether-insoluble bromides. The bromine contents of chloroform soluble and insoluble fractions were 64·92 per cent. and 69·05 per cent. respectively whence the p. c. of chloroform-insoluble bromide (in the ether insoluble bromides) was 13·8. Thus of 31·45 g. of insoluble bromide only 13·8 per cent. was $C_{24}H_{38}O_2Br_{10}$, which was obtainable from 1·34 g. of liquid fatty acids. Hence, the p. c. of $C_{24}H_{38}O_2$ in the liquid fatty acids = 1·34.

Estimation of Linolenic acid $C_{18}H_{30}O_2$ *and Hexadecatrienoic acids* $C_{16}H_{26}O_2$ *in ether insoluble bromides.*

9·41 G. gave chloroform soluble bromides, $C_{18}H_{30}O_2Br_6$ and $C_{16}H_{26}O_2Br_6$, whose bromine contents were 63·32 per cent. and 65·75 per cent. respectively, while that of the mixture was 64·94 per cent. Thus, 66·66 per cent. of the chloroform soluble bromides was $C_{16}H_{26}O_2Br_6$. Hence, of 9·41 g. of liquid acids, 6·13 g. gave benzene-soluble bromide,—*i.e.*, $C_{16}H_{26}O_2Br_6$ and 3·28 g. benzene insoluble bromide—*i.e.* $C_{18}H_{30}O_2Br_6$.

Thus, the p. c. of linolenic acid = 3·28, and that of hexadecatrienoic acid = 6·13.

Estimation of linolenic acid, $C_{18}H_{30}O_2$ *in ether-soluble bromides.*—100 G. of liquid fatty acids gave 12·5 p. c. of ether soluble bromide (Br, 63·32 per cent.). Hence 12·5 g. of bromide were obtained from 4·58 g. of liquid fatty acids. The p. c. of linolenic acid = 4·58.

To sum up:

1. Tetrosapentenoic acid, $C_{24}H_{38}O_2$ = 1·34 per cent.
2. Linolenic acid, $C_{18}H_{30}O_2$.
   (*a*) In ether insoluble bromides = 3·28 per cent.
   (*b*) In ether soluble bromides = 4·58 per cent.
3. Hexadecatrienoic acid, $C_{16}H_{26}O_2$ = 6·13 per cent.
4. Oleic, asellinic and other acids giving liquid bromides = 84·0 per cent.

Total 99·33 per cent.

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Reactivity of Conjugated Systems. Part I. Condensation of Arylidene Ketones with Cyanoacetamide.

By Chittaranjan Barat.

The hypothesis that in a conjugated system of the type $R-CH=CH-CR'=O$, the ethylenic linkage is more reactive than the carbonyl with regard to substances having a reactive methylene group was investigated by Sen and collaborators (*J. Chem. Soc.*, 1915, **107**, 1347; Sen and Basu, *J. Indian Chem. Soc.*, 1927, **4**, 51), who confined their attention mainly to the condensation of hydroxymethylene ketones and β-diketones with cyanoacetamide. (*cf.* also Burdhan, *J. Chem. Soc.*, 1929, 2223). But these constitute conjugated systems that are of a dynamic nature, whereas the case of permanently unsaturated ketones like benzylideneacetone, really belong to a conjugated system of a static nature, and is fundamentally different from the previous type, and hence it would not be unreasonable to suppose that the static conjugated phase included in the second type may behave differently with regard to active methylene groups. With a view to study such reactions, as well as to examine the influence, if any, of the amido-group of cyanoacetamide towards such reactions, the present work was undertaken, the results whereof have been found to throw considerable light on the mechanism of such reactions.

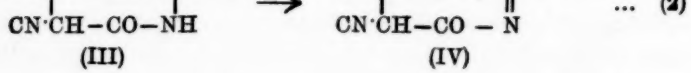
Sen (*loc. cit.*) has only casually mentioned the condensation between benzalacetone and cyanoacetamide, and later similar condensations have been carried out with benzalacetophenone by Kohler and his collaborators (Kohler and Souther, *J. Amer. Chem. Soc.*, 1922, **44**, 2903 ; Kohler, Graustein and Merril, *ibid*, p. 2536) who describe the primary additive compound, obtained in the presence of a trace of sodium ethoxide, as an open-chain amide of the type (I), which suffered loss of a molecule of water and consequent ring closure by the action of dry hydrogen chloride or bromide in an indifferent medium.

$$\begin{array}{l} Ph\cdot CH-CH_2-CO\cdot Ph \\ \quad\quad | \\ CN\cdot CH-CO-NH_2 \\ \quad\quad (I) \end{array} \longrightarrow \begin{array}{l} Ph\cdot CH-CH=C\cdot Ph \\ \quad\quad | \quad\quad\quad | \\ CN\cdot CH-CO-NH \\ \quad\quad\quad (II) \end{array} \quad \ldots (1)$$

In the course of the present work, cyanoacetamide has been condensed with (1) benzalacetophenone, (2) benzal-*p*-methylacetophenone, (3) benzalacetone and (4) α-benzalmethylethylketone both in presence of piperidine or diethylamine (Knoevenagel) and in presence of an equivalent of sodium ethoxide (Michael). It has been found that with Knoevenagel's reagent a product identical with Kohler's primary addition product (I) is obtained, while by Michael's reaction the product becomes identical with Kohler's compound (II); further, the former can be converted into the latter, by the action of gaseous hydrogen chloride (Kohler) or by heating in a sealed tube with an excess of acetic anhydride for 4 to 6 hours at 125° to 150°.

These facts, combined with the results obtained by Kohler and his school, strengthen Sen's view that Knoevenagel's reaction is merely a special case of Michael's universal reaction, and that identical products are obtained at least in the series studied herein whether Michael's or Knoevenagel's reagents are employed.

It has also been observed that the compound obtained by the action of piperidine or diethylamine, is not an open-chain amide, but is a closed-ring piperidine derivative of the type (III), while that obtained with an equivalent quantity of sodium ethoxide belongs to type (IV), and that (III) is converted into (IV) according to the following scheme:—



... (2)

(III) (IV)

The constitution of (III) has been established on the following grounds:—

(*a*) These compounds do not give out ammonia even when warmed with dilute alkalis; on boiling, however, with aqueous alkali the liberation of ammonia becomes perceptible, due to either the rupture of the ring (*vide infra*) or to the hydrolysis of the cyano-group.

(*b*) When treated with sodium ethoxide in boiling alcoholic solution, they do not yield ammonia but sodium salts identical with those obtained by Michael's reaction. Reference will be made to this later.

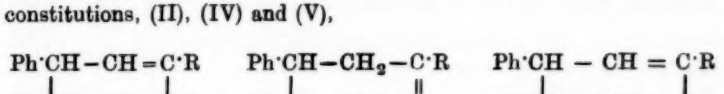
(*c*) They do not yield semicarbazones or oximes, showing the absence of a free ketonic group.

(*d*) Further, the possibility of the existence of a compound of the type (III) is also suggested by the formation of two different iso-

mers, by the employment of piperidine and ammonia respectively. The latter compounds though not yet closely examined, easily yield ammonia on treatment with alkalis, and are hence suspected to belong to type (I).

On these considerations these compounds (Knoevenagel) have here been described as closed-ring piperidine derivatives ; the aldol phase, however, readily eliminates water and as such the isolation of an acyl derivative is naturally not possible. This is strictly in conformity to the expected behaviour of such aldol ring-systems.

A word about the constitution of the tetrahydropyridine derivatives (IV) would not be out of place here. Of the three possible constitutions, (II), (IV) and (V),



(II) (IV) (V)

Kohler and Souther (*loc. cit.*) prefer the structure (II) on account of (*a*) the alleged insolubility of the compound in the strongest alkalis and (*b*) its behaviour towards bromine.

They suggest that a compound of the type (IV) would behave like a saturated ketone towards bromine, which however need not necessarily be true, as bromine is known to be readily taken up by an unsaturated bond between carbon and nitrogen (*cf.* Curtius and Quedenfeldt, *Ber.*, 1895, **28**, 2347 ; *J. pr. Chem.*, 1895, **58**, 385 ; Chattaway and Walker, *J. Chem. Soc.*, 1925, **127**, 979; Hantzsch, *Ber.*, 1890, **23**, 2773 ; James and Judd, *J. Chem. Soc.*, 1914, **105**, 1427). On the other hand they declare compounds of the type (II) to behave like a "completely enolised ketone", and hence respond to Kurt Meyer's method of bromine titration, but it seems to have escaped their notice that these compounds do not give any colouration with alcoholic ferric chloride—a reaction that characterises all enolised ketones—and so the compounds need not possess any enolised phase under ordinary circumstances. It therefore becomes justifiable to conclude that the bromine absorption has nothing to do with the enolic phase of the substances in question. Moreover, as the authors have admitted, the bromination of these compounds is a very complicated affair, as the resulting products are very unstable and readily lose hydrobromic acid resulting in the oxidation of the molecule, and it is extremely difficult to isolate the bromination products

that are primarily formed. A critical examination of the bromination of these compounds is already in progress and would be communicated shortly. Then again, the alleged insolubility of these compounds in alkalis is not general ; thus the tetrahydropyridine derivative obtained from benzalacetone, dissolves in alkalis and is reprecipitated unchanged on acidulation. Moreover, imido-compounds like (II) very frequently possesses a markedly acidic property (*cf.* Sen and Basu, *loc. cit*; also Burdhan, *loc. cit.*) and so the described insolubility of these derivatives in alkalis, instead of supporting their view, serves rather to oppose it.

It must, however, be admitted that such compounds as (IV) may readily tautomerise into compounds of the type (II) and may therefore react in either phase ; but this is not the same thing as saying that (IV) is (II). In view of these considerations, as well as the incapability of these compounds to yield *N*-methyl derivatives on methylation, constitution (IV) seems to be more probable, and has been admitted throughout the course of the present work.

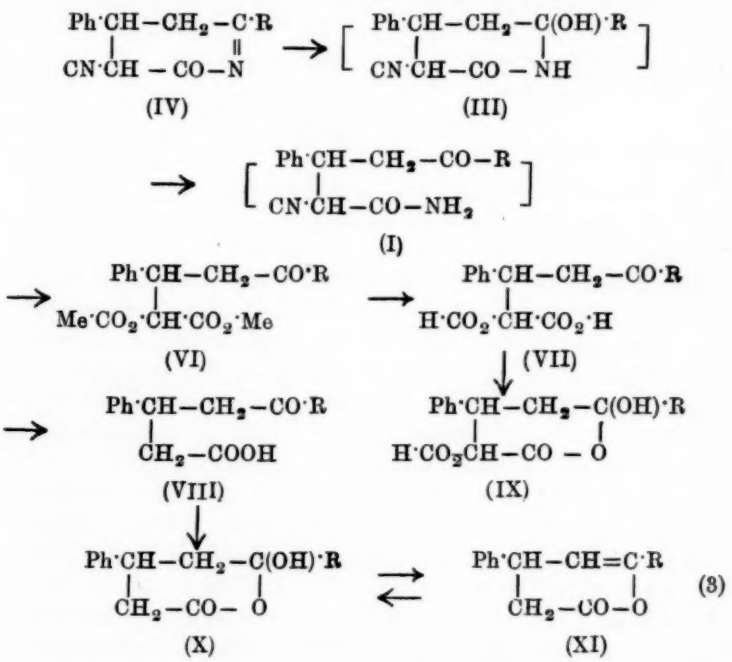
Quite a curious result was, however, obtained when attempting to hydrolyse the cyano-group either in compound (III) or (IV). When heated with concentrated hydrochloric acid in sealed tubes, the ring of these compounds was completely ruptured, resulting in the formation of nitrogen-free open-chain derivatives. When these primary condensation products were treated with concentrated sulphuric acid in the presence of methyl or ethyl alcohols at ordinary temperature, esters of open-chain dibasic acids were obtained. The acids themselves could be obtained by alkaline hydrolysis of these esters, which lost carbon dioxide on melting and yielded compounds identical with those obtained by hydrolysing them with concentrated hydrochloric acid. These monobasic acids crystallise well and correspond to formula (VIII) on analysis, but their properties could not be reconciled to that structure on account of their insolubility in sodium bicarbonate solution even on long keeping, whilst they went into complete solution quite readily in caustic alkalis, and slowly in carbonated alkalis, like lactones; acidulation of the alkaline solutions always gave the original substances back. The presence of a ketonic group was proved by their yielding well-defined oximes and semicarbazones in the usual way. Indirect titration with alkali showed that they behave like monobasic acids.

It is therefore concluded that these compounds undergo the so-called keto-lactol tautomerism, (*cf.* Qudrat-i-Khuda, *J. Chem. Soc.*,

1929, 201) and normally exist in the forms (IX) and (X) respectively which in the presence of substances that tend to anchor either the ketonic or the carboxylic group, assume the forms (VII) and (VIII) and react as di- and mono-basic ketonic acids respectively. It is thus that the formation of semicarbazones and oximes as well as their neutralisation by alkalis is explained.

That these compounds possess a lactol modification is further proved by the formation of an unsaturated lactone (XI) when acted upon by acetyl chloride or acetic anhydride (*cf.* Vorländer and Knotzsch, *Annalen*, 1897, **294**, 333). These unsaturated lactones do not yield semicarbazones or oximes, and are reconverted into the original lactols on warming with aqueous alkalis.

This whole change is represented by the following scheme: –



(3)

The identities of these compounds were further established by synthesising them from the condensation products between the corresponding arylidene ketones and malonic ester in the presence of sodium ethoxide according to the method of Vorländer and his collaborators (*loc. cit.*) when, excepting in the cases of benzalacetone and

α-benzalmethylethylketone (*i.e.*, when R in $Ph{\cdot}CH{=}CH{-}CO{-}R$ contains a primary carbon atom), identical lactols and lactol acids were obtained. When R contains a primary carbon atom, a dihydroresorcinol derivative is obtained, thus:—

$$Ph{\cdot}CH{=}CH{-}CO{\cdot}CH_3 + CH_2{\cdot}(COO{\cdot}Et)_2 \longrightarrow Ph{\cdot}CH(Et{\cdot}CO_2{\cdot}CH{\cdot}CO_2{\cdot}Et){-}CH_2{-}CO{-}CH_3$$

$$\longrightarrow \underset{\text{(XII)}}{Ph{\cdot}CH(Et{\cdot}CO_2{\cdot}CH{-}CO{-}CH_2){-}CH_2{-}CO} + Et{\cdot}OH \longrightarrow$$

$$\longrightarrow \underset{\text{(XIII)}}{Ph{\cdot}CH(H{\cdot}CO_2{\cdot}CH{-}CO{-}CH_2){-}CH_2{-}CO} \longrightarrow \underset{\text{(XIV)}}{Ph{\cdot}CH(CH_2{-}CO{-}CH_2){-}CH_2{-}CO}$$

$$\rightleftarrows \underset{\text{(XV)}}{Ph{\cdot}CH(CH_2{-}C(OH){=}CH){-}CH{=}C(OH)} \qquad (4)$$

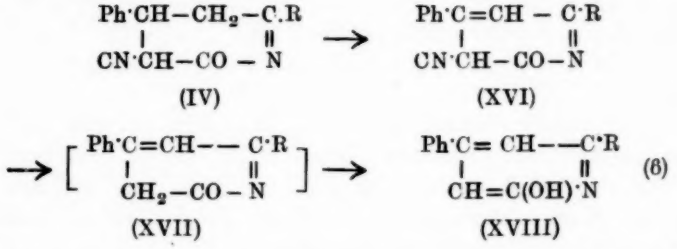
The products do not yield semicarbazones, give colouration with ferric chloride and possess all the properties ascribed to them by Vorländer.

It would thus appear that even in a static conjugated double-bonded system, the addition of the methylene group of cyanoacetamide takes place at the ethylenic linkage and that the amido-group is only helpful in closing the rings through the carbonyl of the conjugated system. The amido-group has no directive influence of its own; acetamide could not be condensed with any of these ketones under the experimental conditions mentioned herein.

The rupture of the pyridine ring appears to be rather improbable but this is due to the extreme instability of partially reduced pyridine rings. To quote Meyer and Jacobson, ("Lehrbuch der Organischen Chemie, 1923, Vol. II, Part III, p. 812). "Interessant sind diese Stoffe (tetrahydro-pyridine) besonders durch die Beziehungen, welche sie mit acyclischen, durch Wasseraufnahme und Ringspaltung aus ihnen gebildeten δ-Amino-ketonen verknüpfen, z. B.:

$$\begin{matrix} CH_2 & --- & CH_2 & --- & CH \\ | & & & & \| \\ CH_2{\cdot}NH{\cdot} & \text{(bzw. NR)} & & & C{\cdot}CH_3 \end{matrix} \quad H_2O \rightleftharpoons \begin{matrix} CH_2{-}CH_2{-}CH_2{-}CO{\cdot}CH_3 \\ | \\ CH_2{-}NH_2 \text{ (bzw. NHR)} \end{matrix} \quad " \qquad (5)$$

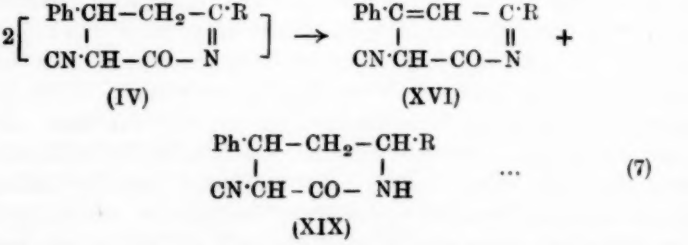
These tetrahydropyridine derivatives contain two hydrogen atoms that are easily removable by bromine (*vide supra*) and by nitrous acid. These dehydrogenated compounds are found to be identical with the condensation products of the corresponding β-diketones and cyanoacetamide (*cf.* Issoglio, *Atti. R. Accad. Sci. Torino*, 1905, **40**, 495; also Basu, *private communication*). Consequently these H-atoms come from the 4th and 5th carbon atoms of the ring. Such a conclusion has found support in the fact (to be described later) that when the hydrogen atom in position 4 is substituted, it is not dehydrogenated either by bromine or by nitrous acid. These compounds are readily hydrolysed by means of 75% sulphuric acid or concentrated hydrochloric acid into known hydroxypyridine derivatives, thus:—



(IV) (XVI)

(XVII) (XVIII) (6)

Further, in the presence of alcoholic ammonia these tetrahydropyridine derivatives undergo reciprocal oxidation and reduction in the following way:—



(IV) (XVI)

(XIX) ... (7)

Such a phenomenon has been known from early times (*cf.* Hantzsch, *Annalen*, 1882, **215**, 370; Paul and Strasser, *Ber.*, 1887, **20**, 2756; Griess and Harrow, *Ber.*, 1888, **21**, 2743; Knoevenagel, *Ber.*, 1902, **35**, 1790; Knoevenagel and others, *ibid*, 1903, **36**, 2813). The results of the present investigation in this line will be shortly communicated.

Kohler and his collaborators have, in their work, noticed many of these points, but their statements lack in conclusive evidence in support of their views and besides, some unfortunate inaccuracies in their work, compelled the present worker to repeat a good many of their experiments before any satisfactory conclusion could be drawn from their statements.

Experimental.

General Method.—The primary condensation and the following conversions were carried out under similar conditions in all the cases cited below, and the general procedure is given here in detail. The yields and other characteristic properties have been given under the respective headings. The cyanoacetamide employed was prepared by the method of Thole and Thorpe, (*J. Chem. Soc.*, 1911, **99**, 422) crystallised from alcohol and dried in vacuum, m.p. 118-20°.

(1) *Michael's Method.*—One atom of sodium was dissolved in a conical flask in just sufficient absolute ethyl alcohol, such that no sodium ethoxide separated on cooling; to this, one molecule of cyanoacetamide similarly dissolved in boiling absolute alcohol was added, when the sodium salt separated out. One molecule of the ketone, dissolved in a little absolute alcohol was then added to this mixture, at about 50°, the flask corked up and the mixture shaken vigorously till the sodium compound went into complete solution; the mixture became warmer and the colour deepened from pale to deep brownish-yellow. In some cases the sodium salt of the reaction product separated in the course of a few hours, while in some, it did so after a day's time. After two days, water was added to the mixture, till the solid went into solution, and the free condensation product was obtained by acidulation with dilute hydrochloric acid. A purer product could be obtained by saturating the alcoholic suspension of the reaction mixture with carbon dioxide when the free condensation product, along with sodium bicarbonate, separated out. The tetrahydropyridine derivative so obtained, was filtered, washed with hot water till free from acids and sodium salts, dried in *vacuo*, and crystallised from alcohol or acetic acid. (The employment of an equivalent quantity of sodium ethoxide did not in any case yield any appreciable quantity of the trimolecular compound described by Kohler).

(2) *Knoevenagel's Method.*—One molecule of cyanoacetamide was dissolved with warming in so much water that it did not separate on cooling, one molecule of the ketone was similarly dissolved in alcohol, the two were mixed in a conical flask, and the mixture made clear by the addition of more alcohol; a little piperidine or diethylamine (usually 1 c.c. for every 4·2 g. of cyanoacetamide) was then added to the mixture, the flask loosely corked and left over, preferably at about 40-50° (an asbestos board on the top of a steam-oven answers the purpose well), when usually the condensation product began to separate in the course of a day or two and became fully separated in one or two weeks. The product was collected, washed with a little rectified spirit and the mother-liquor left over again after the addition of a little more of the amine, when some more condensation product separated in about another week which was again collected in the usual way. Acidulation of the mother-liquor gave some more impure product, unprofitable to recover. The substance was obtained in a sufficiently pure state and could be further purified by crystallisation from alcohol or acetone. This was the hydroxypiperidone derivative (III).

The above compound when dehydrated by a suitable reagent, was nearly quantitatively transformed into the Michael's product. For this purpose the following methods have been employed with success:—

(*a*) By heating the Knoevenagel's condensation product in a sealed tube with an excess of acetic anhydride at 125° to 150° for 4 to 6 hours. The resulting solution was then evaporated to dryness on the water-bath and the residue extracted and crystallised from alcohol.

(*b*) On saturating a chloroform or carbon tetrachloride suspension of the compound with dry hydrogen chloride gas in the cold; the solid first went into solution and then reappeared, as a paste, owing to the separation of water. It was next left to attain the room temperature and then treated with cold water, and neutralised with sodium carbonate. The chloroform or carbon tetrachloride was then removed, the solid collected and purified.

(3) *Hydrolysis of the Condensation Product.*—No general method could be made to answer all the cases under review. The following methods have, however, been employed according to their applicability. As has been referred to already, both Knoevenagel's as well as Michael's condensation products are hydrolysed into the

lactol compounds when subjected to hydrolysis by either of the following ways:—

(*a*) Heating in a sealed tube with 5 to 10% sulphuric acid or with 33% hydrochloric acid converted them directly into the lactol (X) which could be isolated by diluting the solution and separating the so obtained solid; this could then be purified by dissolving in dilute sodium carbonate, filtering and reprecipitating by mineral acids.

(*b*) Dissolving the condensation products in the minimum quantity of cold concentrated sulphuric acid, leaving overnight in a well closed flask (when probably the CN group is converted into the $CO{\cdot}NH_2$ group) and then poured into well cooled methyl or ethyl alcohol, and left again at room temperature for 8 to 10 hours, after which it was treated with cracked ice when the methyl or ethyl ester of the dibasic acid (VII) separated. This when warmed with an excess of 5% aqueous potash, on the water-bath till the whole went into solution, cooled, filtered and acidulated with mineral acids, gave the lactol acid (IX) which could be further purified as above.

These lactol acids lost carbon dioxide on melting, and when kept in a molten state for a few minutes, till the evolution of carbon dioxide ceased, and then cooled, they solidified into beautifully crystalline bodies, identical with the lactols mentioned above.

(4) *Dehydrogenation of the Michael's Condensation Products.*—This could be effected by various ways, of which only the nitrous acid method has been given here in detail. The action of alcoholic ammonia, bromine and hydrogen peroxide would form the subject matter of a future communication.

One molecule of the Michael's condensation product was dissolved in a slight excess of glacial acetic acid and cooled in ice, a little more than two molecules of sodium nitrite dissolved in the minimum quantity of water and well cooled, was then added little by little to the previous solution with good shaking, such that there was no appreciable liberation of NO_2; when all the nitrite solution was added, the flask was left for an hour in the cold, and then allowed to attain the the room temperature and left for about a week. The oxidation product which generally separated out, was then filtered, washed with cold alcohol and crystallised.

(5) *Hydrolysis of the Cyanopyridone Derivatives.*—This could be effected by heating the cyanopyridones either in a sealed tube

with fuming hydrochloric acid at 125—50° for 3 to 4 hours, or by boiling with 75 to 80% sulphuric acid under reflux for 5 to 10 minutes till CO_2 ceased to evolve. The hydrochloric acid hydrolysis product could be isolated by evaporating to dryness on a water-bath, washing the residue with water and crystallising from alcohol. From the sulphuric acid reaction mixture, the product usually separated on dilution, which was filtered, washed free from acid and crystallised from alcohol.

(6) *Condensation of Malonic Ester with Unsaturated Ketones and their Hydrolysis.*—The condensation was carried out exactly as described by Vorländer (*loc. cit.*). The mixture was left over for a day at room temperature, diluted with water, the aqueous solution washed with ether to remove any unchanged ketone or ester, and acidulated by dilute hydrochloric acid when the condensation product usually separated as a paste which solidified on cooling and scratching. This was then hydrolysed with excess of 5% aqueous potash in the usual way, when the corresponding lactol acid (IX) or the dihydroresorcinol derivative was obtained. The lactol acid could be converted into the corresponding lactol by heating. When this lactol was dehydrated with acetyl chloride or acetic anhydride, it was converted into the unsaturated lactone (XI). On treatment with aqueous potash and subsequent acidulation of the solution the original lactol was regenerated.

The dihydroresorcinol derivatives obtained from benzalacetone or α-benzalmethylethylketone, on boiling under reflux with an excess of barium hydroxide solution, containing 2½ times their weight of $Ba(OH)_2$ were converted into the lactol acid (IX) which on melting, formed the lacol (X) identical with those obtained from the corresponding cyanoacetamide condensation products.

I. *Condensation of Benzalacetophenone with Cyanoacetamide.*

Benzalacetophenone was prepared by the method of Kohler and Chadwell ("Organic synthesis" II, 1). Yield 90%; m.p. 55-6°.

(1) *By Michael's method:—Formation of 2-keto-3-cyano-4:6-diphenyl-2:3:4:5-tetrahydropyridine.*—The sodium salt of the condensation product began to separate within a couple of hours, and was completely separated in a day or two, and separation of the condensation product by mineral acids gave a fairly pure product, yield being about 87%. It was fairly soluble in the alcohols, pyridine

and acetic acid, sparingly so in ether and benzene, and almost insoluble in chloroform and petroleum ether. It was insoluble in dilute acids or alkalis, soluble in strong sulphuric acid, gave no coloration with ferric chloride. It crystallised from acetic acid or alcohol in small prisms; m. p. 220-22°. (Found : C, 78·35; H, 5·28; N, 10·43. $C_{18}H_{14}ON_2$ requires C, 78·83; H, 5·11; N, 10·22 per cent.).

(2) *By Knoevenagel's method*:—*Formation of 2-keto-3-cyano-4:6-diphenyl-6 hydroxypiperidine.*—The mixture began to deposit the condensation product in a day, and about 75% of the theoretical quantity could be obtained after a week. It was fairly soluble in the alcohols, acetone and acetic acid, sparingly so in ether, benzene and chloroform and insoluble in petroleum ether; insoluble in dilute alkalis and acids, soluble in strong sulphuric acid; gave no coloration with ferric chloride. It crystallised from methyl alcohol or acetone in colourless prismatic needles, m. p. 161-62°. (Found: C, 73·61; H, 5·56; N, 9·33. $C_{18}H_{16}O_2N_2$ requires C, 73·97; H, 5·48; N, 9·59 per cent.).

This compound on treatment with dry hydrogen chloride in chloroform suspension or on heating with an excess of acetic anhydride in a sealed tube at 120-25° for 6 hours was converted into the Michael's compound, identified with a specimen from stock.

(3) *Hydrolysis of the condensation products*:—*Formation of dimethyl ester of α-carboxy-β-phenyl-γ-benzoylbutyric acid, and the corresponding lactol acid and lactol.*—

(*a*) The methyl ester crystallised from dilute methyl alcohol as white prismatic needles, m. p. 108°, very soluble in all common organic solvents. (Found: C, 70·41; H, 6·06. $C_{20}H_{20}O_5$ requires C, 70·59; H, 5·88 per cent.).

(*b*) The lactol acid was obtained in an yield of 60% by hydrolysing the above ester. It was very soluble in all organic solvents excepting petroleum ether and benzene. Crystallised from benzene with a few drops of methyl alcohol, it came in fine short white needles, m. p. 152-4° with decomposition; it dissolved freely in alkalis, carbonates and bicarbonates from which it was precipitated unchanged on acidulation. (Found: C, 68·97; H, 5·33. $C_{18}H_{16}O_5$ requires C, 69·23; H, 5·13 per cent.). 0·2050 G. of the substance required 12·9 c.c. of *N*/10-alkali for neutralisation showing it to be a dibasic acid.

(*c*) The lactol was obtained in a nearly theoretical yield when the above compound was kept in a molten state till effervescence

ceased. On cooling, the pale yellow melt solidified in long needles; it was fairly soluble in all common solvents, and crystallised from methyl alcohol in beautiful colourless needles, m. p. 158°. It dissolved readily in caustic alkalis, slowly in carbonates and was insoluble in bicarbonate solution. This compound could be directly obtained when either of the original condensation products were heated with about 10 times their weight of strong hydrochloric acid in a sealed tube for 6 hours at 125° and treated as usual. (Found: C, 75·84; H, 6·19. $C_{17}H_{16}O_3$ requires C, 76·12; H, 5·94 per cent.). 0·1206 G. of the substance required 4·4 c.c. of $N/10$-alkali, corresponding to a monobasic acid. The semicarbazone, obtained as usual melted with decomposition at 215°.

(4) *Formation of 3-cyano-4:6-diphenyl-2-pyridone.*—The compound separated completely during the course of about a week when it was filtered off, washed with alcohol, dried and crystallised from glacial acetic acid, or a mixture of equal volumes of pyridine and alcohol (charcoal) as pale yellow prismatic needles, m.p. 320° (Kohler gives it to be 313-15°). It was found to be identical with a specimen obtained by the condensation of cyanoacetamide with dibenzoyl methane (Basu, *private communication*). Was very sparingly soluble in all common organic solvents, excepting glacial acetic acid and pyridine. It dissolved in alkalis, and in strong sulphuric acid; gave no coloration with alcoholic ferric chloride. (Found: N, 10·12. $C_{18}H_{12}ON_2$ requires N, 10·30 per cent.).

(5) *Hydrolysis of the Cyanopyridone: —Formation of 2-hydroxy-4:6-diphenylpyridine.*—The hydrolysis could be best effected by taking the cyanopyridone (1 g.) in 75 per cent. sulphuric acid (10 c.c.) in which it dissolved giving a yellow solution, and boiling it for about 5 to 10 minutes, till the evolution of CO_2 ceased. On cooling and diluting, the hydroxypyridine separated as a yellow solid which crystallised from rectified spirit as pale yellow needles, m.p. 208° (Kohler gives 210°). This was identified with a sample obtained by the hydrolysis of the condensation product between dibenzoylmethane and cyanoacetamide. It was very soluble in all common organic solvents, excepting petroleum ether. It dissolved in alkalis from which it was reprecipitated unchanged on acidulation and gave a brownish red colouration with ferric chloride. (Found: N, 5·79. $C_{17}H_{13}ON$ requires N, 5·66 per cent.).

(6) *Condensation with malonic ester:—Formation of diethyl ester of α-carboxy-β-phenyl-γ-benzoylbutyric acid.* The ester was

obtained in the usual way. Yield was equal to the weight of the ketone employed; crystallised from methyl or ethyl alcohol it was obtained as colourles needles, melting at 150°. (Found: C, 72·01; H, 6·83. $C_{22}H_{24}O_5$ requires C, 71·74; H, 6·52 per cent.). On hydrolysis with aqueous KOH, the lactol acid m.p. 152-4° was obtained (Vorländer and Knotzsch, m.p. 144°). This was converted into the corresponding lactol by heating; m.p. 158° (Vorländer and Knotzsch, m.p. 155-56°; oxime, m.p. 144-46°). These were found to be identical with the corresponding compounds obtained from the tetrahydropyridine derivatives. The unsaturated lactone obtained by dehydration as usual, crystallised from ether or petroleum ether, m.p. 58°; on heating with aqueous alkalis it regenerated the original lactol.

II. *Condensation of Benzal-p-methylacetophenone with Cyanoacetamide.*

Benzal-p-methylacetophenone was prepared in the same way as benzalacetophenone, only about twice the volume of alcohol had to be employed and the mixture had to be left for about a week, before the unsaturated ketone could be obtained in a solid state. Yield about 80 per cent. After crystallisation from alcohol it was obtained in lemon-yellow crystals melting at 75°.

(1) *By Michael's method*:—*Formation of 2-keto-3-cyano-4-phenyl-6-p-tolyl-2:3:4:5-tetrahydropyridine.*—It was obtained by hydrochloric acid separation in an yield of about 90 per cent. of theory. Crystallised from alcohol it was obtained in light white clusters of soft needles, m.p. 185°; excepting for its better solubility it resembled its lower homologue in all other properties. (Found: N, 9·78. $C_{19}H_{16}ON_2$ requires N, 9·73 per cent.).

(2) *By Knoevenagel's method*:—Formation of *2-keto-3cyano-4-phenyl-6-p-tolyl-6-hydroxypiperidine.*—The condensation product separated during the course of three or four days, yield 75 per cent. crystallised from dilute acetone it came as a light white powder, m.p. 230°. (Found: N, 8·98. $C_{19}H_{18}O_2N_2$ requires N, 9·15 per cent.). This compound could be quantitatively transformed into the tetrahydropyridine derivative as in the previous case.

(3) *Hydrolysis of the condensation products.*—These changes could be effected in an exactly similar way as in the previous case.

(*a*) *Dimethyl ester of α-carboxy-β-phenyl-γ-p-toluyl butyric acid* resembled the corresponding γ-benzoyl derivative in all properties but was more soluble than it. Crystallised from methyl alcohol it

melted at 95°. (Found: C, 70·87; H, 5·93. $C_{21}H_{22}O_5$ requires C, 71·18; H, 6·21 per cent.).

(*b*) The lactol acid obtained and crystallised as before melted at 150° with decomposition. (Found: C, 70·21; H, 5·79. $C_{19}H_{18}O_5$ requires C, 69·94; H, 5·52 per cent.). 0·1096 G. of the acid required 6·4 c.c. of *N*/10-alkali, indicating it to be dibasic.

(*c*) The lactol obtained either by heating the above compound or by direct hydrolysis of the original condensation products by concentrated hydrochloric acid in a sealed tube was obtained as fine colourless needles that melted at 175°. (Found: C, 76·07; H, 6·63. $C_{18}H_{18}O_3$ requires C, 76·60; H, 6·38 per cent.). 0·0536 G. of the substance required 1·9 c.c. of *N*/10-alkali, corresponding to a monobasic acid of the same formula. The semicarbazone obtained as usual, melted at 222°, with decomposition.

(4) *Formation of* 3-*cyano*-4-*phenyl*-6-p-*tolyl*-2-*pyridone*.—The compound was obtained similarly as in the previous case, yield about 60-70 per cent. Crystallised from glacial acetic acid (charcoal) it was obtained in pale yellow needles, m.p. 268°. (Found: N, 9·78. $C_{19}H_{14}ON_2$ requires N, 9·78 per cent.).

(5) *Formation of* 2-*hydroxy*-4-*phenyl*-6-p-*tolylpyridine*.—The above on hydrolysis with 80 per cent. sulphuric acid gave the hydroxypyridine in an yield of about 90 per cent. Crystallised from rectified spirit (charcoal) it came as light yellow needles, m.p. 226-28°; it was soluble in alkalis, gave a brownish red coloration with ferric chloride. (Found: N, 5·46. $C_{18}H_{15}ON$ requires N, 5·36 per cent.).

(6) *Condensation with malonic ester*.—(*a*) The diethyl ester obtained as before crystallised from methyl alcohol and resembled the lower homologue in all its properties, m.p. 123°. (Found: C, 71·98; H, 6·63. $C_{20}H_{26}O_5$ requires C, 72·25; H, 6·81 per cent.).

(*b*) The lactol acid crystallised from benzene containing a little methyl alcohol melted at 150° with decomposition forming the lactol.

(*c*) The lactol when crystallised from rectified spirit melted at 175°; both these compounds were identified with the corresponding compounds obtained from the cyanoacetamide condensation products.

(*d*) The unsaturated lactone was obtained by the action of acetic anhydride as usual. Crystallised from ether in long needles it melted at 98°; on boiling with aqueous alkali it was reconverted into the original lactol.

III. *Condensation of Benzalacetone with Cyanoacetamide.*

The ketone was obtained from the market. It was not found necessary to recrystallise it and so it was used as obtained.

(1) *Michael's reaction:—Formation of 2-keto-3-cyano-4-phenyl-6-methyl-2:3:4:5-tetrahydropyridine.*—The sodium salt of the condensation product separated more slowly in this case, the completion of the reaction requiring about 3 to 4 days. The condensation product was separated by carbon dioxide, filtered, washed with a little alcohol and finally with hot water. The alcoholic solution gave a further quantity on concentration, the total yield being about 65 per cent. It dissolved in alkalis, from which it was obtained unchanged on acidulation; was very soluble in pyridine and acetic acid, less so in the alcohols, acetone and benzene, and insoluble in petroleum ether and water. It crystallised from hot amyl or ethyl alcohol in fine colourless prisms, melting at 267° and darkening a few degrees earlier. (Found: N, 13·59. $C_{13}H_{12}ON_2$ requires N, 13·20 per cent.).

(2) *Knoevenagel's method:—Formation of 2-keto-3-cyano-4-phenyl-6-methyl-6-hydroxypiperidine.*—The reaction took about a fortnight to 3 weeks for completion; total yield about 60 per cent. Moderately soluble in the alcohols, acetone and water, more so in acetic acid and pyridine, insoluble in benzene and petroleum ether. Soluble in dilute alkalis and acids by virtue of its solubility in water. It crystallised from alcohol or water in colourless needles melting with decomposition at 195-96°. (Found: N, 12·33. $C_{13}H_{14}O_2N_2$ requires N, 12·17 per cent.). For conversion into the tetrahydropyridine derivative it required a little longer keeping with gaseous hydrochloric acid in carbon tetrachloride suspension (half to one hour at room temperature) as well as longer heating (8 to 10 hours at 125-30°) with acetic anhydride than in the previous cases. The products of both treatment were identical with the Michael compound.

(3) *Hydrolysis of the condensation products.* The lactol was directly obtained by heating either of the condensation products with an excess of 5 per cent. sulphuric acid in a sealed tube at 125-30° for 6 to 8 hours when it separated as a heavy oil, which solidified on ice-cooling and scratching. It was purified as usual and crystallised from a mixture of petroleum ether and benzene in white granular crystals, m.p. 85°. (Found: C, 69·72; H, 7·07. $C_{12}H_{14}O_3$ requires

C, 69·9; H, 6·8 per cent.) 0·1364 G. of the substance required 6·6 c.c. of *N*/10-alkali corresponding to a monobasic acid of the same composition. Its semicarbazone, obtained in the usual way, melted at 170° with decomposition. On treatment with acetic anhydride it gave an oily product, which regenerated the original lactol on heating with aqueous alkalis.

(4) *Formation of 3-cyano-4-phenyl-6-methyl-2-pyridone.*—The dehydrogenation product did not separate even on considerable dilution of the reaction mixture. It separated as a light brown powder on neutralising the acetic acid by sodium carbonate. It crystallised from acetic acid in fine needles that melted at 275°-76°. Identified with a sample of 3-cyano-4-phenyl-6-methyl-2-pyridone prepared by Basu (*private communication*). It was soluble in most organic solvents and also somewhat in water; it dissolved in dilute alkalis quite readily, but did not give any colouration with ferric chloride. (Found: N, 13·53. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.).

(5) The above could be readily hydrolysed into *2-hydroxy-4-phenyl-6-methylpyridine* by either of the hydrochloric acid or sulphuric acid methods. It crystallised from alcohol in fine needles, melting at 206-7° and possessed all the properties ascribed to it by the previous authors.

(6) Condensation with malonic ester, gave the dihydroresorcinol derivative described by Vorländer (*loc. cit.*). This was converted into the corresponding lactol (described by Vorländer as *β-phenyl-γ-acetylbutyric acid* m.p. 84°; oxime, m.p. 127°) by boiling with barium hydroxide, followed by subsequent heating; crystallised from a mixture of petroleum ether and benzene, it melted at 85° and was identified with the specimen obtained from the corresponding cyanoacetamide condensation product.

IV. *Condensation of α-Benzalmethylethylketone with Cyanoacetamide.*

The ketone was prepared by the method of Harries and Müller, (*Ber.*, 1902, **35**, 968, 971) supplemented by the modification of Drake and Allen, jr. ("Organic Synthesis" II, 17); b.p. 225-30°/15 mm. Yield 60 per cent.

(1) *By Michael's reaction:—Formation of 2-keto-3-cyano-4-phenyl-6-ethyl-2:3:4:5-tetrahydropyridine.*—The sodium salt of

the condensation product did not separate as happened in the other cases; separation of the free condensation product was best effected by CO_2, yield about 60 per cent. It was fairly soluble in alcohol, acetic acid aud pyridine, sparingly so in benzene and acetone and insoluble in petroleum ether and water. Crystallised from rectified spirit, it melted at 178-80°; and resembled its lower homologue in other properties. (Found: N, 12·12. $C_{14}H_{14}ON_2$ requires N, 12·39 per cent.).

(2) *By Knoevenagel's reaction*:—*Formation of 2-keto-3-cyano-4-phenyl-6-ethyl 6-hydroxy-piperidine.*—Obtained as usual, the yield barely reaching about 45 per cent. sparingly soluble in alcohol and benzene, moderately so in acetone, insolubie in petroleum ether and water and very soluble in acetic acid. Crystallised from dilute acetone it melted with decomposition at 235-36°. (Found: N, 11·83. $C_{14}H_{16}O_2N_2$ requires N. 11·48 per cent.). It could be converted into the Michael compound in the usual way.

(3) *Hydrolysis of the condensation products.*—The lactol was directly obtained by hydrolysing either of the condensation products by heating in a sealed tube with 10 per cent. sulphuric acid at 140-150° for 6 hours. It was very soluble in most solvents, crystallised from benzene, it melted at 108°, and resembled the other members of the series. (Found: C, 70·67; H, 7·51. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·27 per cent.). 0·1038 G. of the substance neutralised 4·9 c.c. *N*/10-alkali showing it to be monobasic. The unsaturated lactone was obtained as an uncrystallisable oil, which on heating with aqueous alkalis gave the original lactol back. Semicarbazone, obtained as usual, melted at 165° with decomposition.

(4) *Dehydrogenation* by means of nitrous acid gave a product that separated only on dilution of the reaction mixture; *3-cyano-4-phenyl-6-ethyl-2-pyridone* separated from dilute acetic acid in prisms melting at 268°. (Found: N, 12·67. $C_{14}H_{12}ON_2$ requires N, 12·50 per cent.).

(5) The *hydrolysis* of the above compound was effected by means of 75 per cent. sulphuric acid as usual; *2-hydroxy-4-phenyl-6-ethylpyridine* was obtained in fine needles from alcohol, melting at 165° and resembled the other members of this series in all other respects. (Found: N, 7·26. $C_{13}H_{13}ON$ requires N, 7·04 per cent.).

(5) *Condensation with malonic ester* gave rise to a dihydroresorcinol derivative. The dihydroresorcyl ester was obtained as

usual and crystallised from rectified spirit in large colourless prisms that gradually become yellowish on keeping, melting at 120°. (Found: C, 69·89; H, 6·65. $C_{16}H_{18}O_4$ requires C, 70·01; H, 6·57 per cent.). The *dihydroresorcinol* was obtained in the same way as in the preceding case which crystallised from rectified spirit in small yellowish granular prisms melting at 214°. (Found: C, 76·98; H, 7·14. $C_{13}H_{14}O_2$ requires C, 77·22; H, 6·93 per cent.). This was converted into the corresponding *lactol* in the same way as above and identified with that obtained from the cyanoacetamide condensation product, m.p. 108°.

In conclusion, I wish to express my sincere thanks to Professor H. K. Sen, for his keen interest in this investigation and for placing the resources of his laboratory at my disposal. My thanks are also due to Messrs. I. B. Sen-Gupta and U. Basu for valuable assistance rendered in course of this work.

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Studies in Silicic Acid Gels. Part IV. The Effect of Electrolytes on the Time of Setting of the Gel-forming Mixtures.

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It has been shown in Part II (Prasad and Hattiangadi, *J. Indian Chem. Soc.*, 1929, **6**, 893) that the process of setting of mixtures of solutions of sodium silicate and acidic ammonium acetate or acetic acid consists of three stages:

(1) The formation of silicic acid by the interaction of acids with sodium silicate.

(2) The formation of the colloidal solution of silicic acid.

(3) The coagulation of the colloidal solution by the electrolytes liberated in the first reaction.

The present investigation was undertaken with a view to examine the effect produced on the time of setting of the silicic acid gels by the addition of extra quantities of electrolytes to the gel-forming mixtures.

Experimental.

The effect of sodium and potassium salts of nitric, sulphuric, hydrochloric and acetic acids on the acid and alkaline gel-forming mixtures has been chiefly studied. The effect of bivalent and trivalent basic radicles could not be examined as most of these electrolytes reacted to give the corresponding insoluble silicates. The electrolytes used were Merck's "extra pure" chemicals.

The sodium silicate used was Na_2O, $2SiO_2$ and a solution of 4 per cent. silica content was prepared as described in Part I (*cf.* Prasad and Hattiangadi, *J. Indian Chem. Soc.*, 1929, **6**, 653). It was observed during the course of this investigation that the nature of sodium silicate (*cf.* Harmann, *J. Phys. Chem.*, 1925, **29**, 1155; 1926, **30**, 359, 917) is very important in studying the process of gel-formation. A solution of 4 per cent. silica content of sodium silicate Na_2O, SiO_2 could not give rigid gels with ammonium acetate or acetic acid like Na_2O, $2SiO_2$ even when the p_H of the reaction mix-

ture was 8·5—9. With Na_2O, SiO_2, in fairly alkaline solutions, only a flaky precipitate was produced which settled to the bottom on standing. Highly alkaline solutions hardly showed any signs of coagulation even in course of weeks. Pyridine, which has been shown in Part III to accelerate the process of gelation tremendously, failed to produce a stiff gel in fairly alkaline solutions. A stiff gel is however obtained near the neutralisation point when the reaction mixture is just alkaline, that is, when the process of gelation is quickest and there is hardly any time for a possible peptisation of the coagulum formed. Of course, in acidic mixtures stiff vibrant gels with solutions of Na_2O, SiO_2 were easily obtained. Besides these deviations, the sample Na_2O, SiO_2 dissolved in water easily, the process of solution being highly endothermic, while Na_2O, $2SiO_2$ and Na_2O, $2{\cdot}33SiO_2$ took a long time to give clear solutions and the absorption of heat during solution was negligible.

In the following, different amounts of 4*N*- and 2*N*-electrolytes were added to 5 c.c. of the acetic acid solution and this was mixed with 5 c.c. of the solution of sodium silicate (Na_2O, $2SiO_2$). The time of setting was measured from the time—deflection curves (*cf.* Part I, *loc. cit.*) and the results obtained are given in the following tables.

TABLE I.

Concentration of SiO_2 = 4 per cent.
Concentration of acetic acid = 0·8*N*.

Reaction acidic.

Electrolytes.	C.c. of 4*N*-electrolytes in 10 c. c. of the mixtures.							
	0		0·5		1·0		1·25	
	t (min.)	A	t (min.)	A	t (min.)	A	t (min.)	A
NaCl	57	5·5	42	6	32	6·5	29	7·0
KCl	57	5·5	36	6	24	7·5	20	8·0
$NaNO_3$	57	5·5	48	6	36	6·5	30	6·5
KNO_3	57	5·5	38	6	27	7·0	24	7·5
NaAc	57	5·5	39	6	32	7·0	30	7·5
KAc	57	5·5	34	7	25	7·5	23	7·5
Na_2SO_4	57	5·5	50	5·5	45	6·0	43	6·0

TABLE II.

Concentration of SiO_2 = 4 per cent.
Concentration of acetic acid = 0·55*N*.

Reaction alkaline.

	C.c. of 2*N*-electrolytes in 10 c. c. of the mixtures.					
	0		1·0		2·5	
Electrolytes.	t (min.)	A	t (min.)	A	t	A
NaCl	22	9	3	20	45 sec.	30
KCl	22	9	1½	24	Ppt.	—
$NaNO_3$	22	9	3½	17	1 min.	28
KNO_3	22	9	2	21	20 sec.	30
NaAc	22	9	3	22	40 sec.	32
KAc	22	9	1½	25	Ppt.	—
Na_2SO_4	22	9	6	17	2 min.	22

It will be seen from Tables I and II that the addition of extra quantities of electrolytes accelerates the gel-formation in the alkaline and the acid mixtures. Increasing quantities of the substances not only reduce the time of setting but also increase their opacity. It will further be seen that the size of the gel particles is different with different electrolytes and is not dependent upon the time of setting as shown in column A of the tables.

The effect of these substances on the pure dialysed sol of silicic acid was then examined and no evidence of coagulation could be detected. This observation is similar to that of Thomas Graham (*J. Chem. Soc.*, 1864, **17**, 321) who found that acids were inactive towards a pure sol of silicic acid.

The pure dialysed sol was made alkaline and acidic by the addition of sodium hydroxide and hydrochloric acid respectively. The effect of the addition of these electrolytes to these alkaline and acid sols was that a rapid coagulation took place in the former, while hardly any coagulation was observed in the latter. Pappada (*Gazzetta*, 1905, **35**, 78; *J. Chem. Soc., Abs.*, 1905, *ii*, **88**, 387) also found that coagulants were rendered inactive in the presence of acids while coagulation was favoured in the presence of substances having a basic reaction and that the coagulating action of salts is intimately connected with the position of the metals in the periodic system.

Discussion of Results.

The addition of extra quantities of electrolytes to these gel-forming mixtures corresponds to the case of coagulation of a colloidal solution by mixtures of electrolytes.

Freundlich, Weiser, Dhar, Mukherjee and others have studied the coagulation of colloidal solutions by mixtures of electrolytes and have found that various factors, such as hydration of the ions and of the colloid, the displacement of adsorption of one ion by the other, the variation of the electric charge on the colloid, come into play.

The results of the present investigation on the influence of other electrolytes in the presence of sodium acetate on the coagulation of the silicic acid sol indicate the order of coagulating power as follows:—

$$KAc > NaAc;\ KCl > NaCl;\ KNO_3 > NaNO_3,$$

both in the alkaline and in the acid media. The state of aggregation of the gel particles is also in the same order. This is in confirmation with the observation of Pappada (*loc. cit.*) who found the order Cs> K>Na>Li as regards their coagulating power on the silicic acid sol.

It is also evident from the above results that the influence of the anions on the gel-formation is in the order $Cl > NO_3 > SO_4$. The state of aggregation of the gel particles also follows the same order. Dokan's (*Kolloid Z.*, 1924, **34**, 155) recent work on the swelling of agar-agar also suggests that the state of aggregation of the gel colloids and coherence of their frame work is influenced by the nature of the electrolytes. To examine the behaviour of these ions further, gels were prepared only from sodium silicate (Na_2O, $2{\cdot}33SiO_2$) and NH_4Cl, NH_4NO_3, and $(NH_4)_2SO_4$, and the following results were obtained for the time of setting measured by Fleming's method.

It may be mentioned here that very good gels can be obtained easily, by using almost any ammonium salt instead of ammonium acetate.

TABLE III.

Concentration of SiO_2=4 per cent.

	NH_4Cl	NH_4NO_3	$(NH_4)_2SO_4$
Strength.	t	t	t
0·5*N*	17 min. 20 sec.	87 min.	4 hrs.
0·6*N*	4 ,, 40 ,,	11½ ,,	28½ min.
0·7*N*	1 ,, 20 ,,	3½ ,,	7½ ,,

TABLE III—*contd.*

Concentration of SiO_2=5 per cent.

	NH_4Cl	NH_4NO_3	$(NH_4)_2SO_4$
Strength.	t	t	t
0·7*N*	1 min. 45 sec.	5 min.	14 min.

Concentration of SiO_2=3 per cent.

0·6*N*	1 min. 10 sec.	3 min.	6 min.

These results confirm the conclusion arrived at above that the power of decreasing the time of setting is in the order $Cl > NO_3 > SO_4$.

The acetates seem to have a marked coagulating influence. Werner (*J. Amer. Pharm. Assoc.*, 1920, **9**, 501) found that the acetates of the various metals had the greatest congealing effect on the silicic acid sol. It appears from similarity of the results obtained in this investigation with those obtained by Werner, Graham, Pappada and others (*loc. cit.*) that gel-formation is really a case of coagulation of the colloidal silicic acid by electrolytes. The great effect of the acetates in the present case may also be due to a repression of the H- and OH-ions, thus making the silicic acid sol formed in the gel-forming mixtures of sodium silicate and acetic acid comparatively unstable.

The behaviour of sodium sulphate in being a poor coagulant is rather anomalous. In the acid region where the silicic acid particles are positively charged, the sulphate ion should be a better coagulant than the other monovalent anions. This observation is similar to that pointed out in Part II that with sulphuric acid the time of setting is greater in the acidic as well as alkaline media than with hydrochloric acid in mixtures of the same p_H. It is probable that this is a case of ionic antagonism.

Kruyt and Postma (*Rec. trav. chim.*, 1925, **44**, 765) have found that large quantities of OH- and Cl-ions are adsorbed by silicic acid whether positively or negatively charged. The better congealing effect of the chloride than the nitrate, perhaps, depends upon the preferential adsorption of the Cl-ions. The Cl-ions do not, it appears, stabilise the silicic acid sol in the alkaline medium, as would

be expected from the ordinary laws of coagulation. OH-Ions also behave in a similar manner, that is, instead of stabilising the negetively charged sol, the slightest excess of them causes a turbidity and favours strong flocculation or complete gelatinisation by other electrolytes.

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Composition of Jute Fibre. Part II. Hemicelluloses.

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It is generally assumed that jute cellulose is associated with "hemicelluloses"—pentosans, hexosans or hexopentosans, which are generally insoluble in water but soluble in alkali and are readily hydrolysed by acids. No precise information as to the nature of these carbohydrates accompanying jute cellulose is however available. The following investigations were undertaken with the object of obtaining a peep into the nature of so-called hemicelluloses in jute.

In order to avoid complications due to the presence of lignone matter, it is necessary to free the fibre from the last traces of lignone. Different investigators who studied hemicelluloses in wood, straw or other lignocelluloses, delignified their fibres by the usual methods of treatment with bisulphite, alkali or chlorine. All these delignifying agents however not only remove a considerable portion of hemicelluloses but affect them chemically as well. For satisfactory investition of hemicelluloses, a reagent is necessary which, while removing the lignone matter completely, would leave the non-celluloses intact.

In a previous communication (*J. Indian Chem. Soc.*, 1929, **6**, 339) it was found that hemicelluloses remained practically unaffected when jute fibre was delignified with 2·5% chlorine peroxide solution. Jute lignone was completely oxidised by this reagent into water-soluble products which could be easily washed off.

Delignification by Chlorine Peroxide.—It has been found that delignification is effected more efficiently by the action of chlorine peroxide *gas* on moist jute instead of its solution in water or acetic acid as recommended by Schmidt and Graumann (*Ber.*, 1921, **54**, 1860). To remove lignone completely, either a single exposure for two or three days or two exposures, each of twenty-four hours' duration, to a slow stream of chlorine peroxide gas have been found most effective. A slow stream of chlorine peroxide may easily be obtained by the action of dilute sulphuric acid on potassium chlorate and oxalic acid at room temperature (25-30°) with slight previous heating. If sodium chlorate is used in place of the potassium salt, more dilute acid has to be used while the slight previous warming may be dispensed with. The process goes on smoothly, without any attention as

regards the control of temperature, strength of solution and other factors while the worker is saved from the danger of exposing himself to the highly irritating fumes of chlorine peroxide when handling the solution. The tedious process of obtaining a concentrated solution of the gas in ice-cooled water may thus be avoided. Delignification is also more effective while the furfural-yielding complexes are left practically intact.

Extraction of Hemicelluloses.—The delignified jute was extracted successively with (*a*) benzene. (*b*) 95% alcohol, (*c*) boiling water, and (*d*) 17·5% caustic soda. The extracted material was then isolated either by evaporation of the solvent or by concentration and addition of alcohol. The hemicelluleses thus obtained were purified by repeated precipitation with alcohol from their solutions. The solid substances were then hydrolysed with sulphuric acid (2·5%), and the excess of the acid removed as barium sulphate. The filtrate was then concentrated under reduced pressure to a syrup which was tested for different carbohydrates and was also used for their quantitative estimation.

Carbohydrates found in the Hemicelluloses.

Galactose.—For the detection and estimation of galactose in the presence of galacturonic acid, the oxidation method was found to be unsuitable, as both the substances gave mucic acid on oxidation. A satisfactory separation was however effected by the insolubility of barium galacturonate in 80% alcohol which however dissolved galactose (O'Dwyer, *Biochem. J.*, 1926, **20**, 656).

Schmidt and others (*Cellulosechem.*, 1929, **10**, 126) investigated the presence of galactose in different cellulose materials but in all cases it was found absent. This was perhaps due not to the actual absence of galactose in the original material but to the fact that galactose, linked with galacturonic acid, was easily removed by sodium sulphite treatment to which they subjected the delignified fibres.

Fructose.—Fairly large amount of fructose (6·3% in the alkali extract) has been found present in jute. This has been confirmed by a large number of qualitative tests and estimated in the presence of aldoses by the method of Willstätter and Schüdel (*Ber.*, 1928, **51**, 780).

"Uronic" Acids.—Attention is due to the large amount of "uronic" acids (*e.g.*, galacturonic acid) in different fractions. Galacturonic

acid reduces Fehling's solution readily and gives all the colour reactions for pentoses and probably for this reason its presence in ligno-celluloses has escaped notice. It was first assumed that the large amount of uronic acids found in these experiments were due to the oxidising action of chlorine peroxide on jute. This was however found not to be the case; for, the furfural content and uronic acids of jute were 10·06% and 8·08% respectively, while those of the delignified fibre were 8·8% and 9·01% (calculated on jute) respectively. It is therefore evident that neither the furfural-yielding complexes nor the uronic acids were seriously affected by the action of chlorine peroxide.

Galacturonic acid has been identified by qualitative tests. Attempts were made to estimate it by the following methods:

(1) Direct titration with alkali.

(2) Oxidation to mucic acid.

(3) Estimation of carbon dioxide evolved by treatment with 12% hydrochloric acid (Tollens and Le Fevré, *Ber.*, 1907, **40**, 4513; Nanji, Paton and Ling, *J. Soc. Chem. Ind.*, 1925, **44**, 253T).

The titration method was found unsatistactory as it did not give concordant results in all cases while the mucic acid method could not be applied owing to the presence of galactose. Estimation of carbon dioxide was however found quite satisfactory and this method has been therefore used in these experiments. The amounts of uronic acids (calculated as galacturonic acid) found in different fractions are stated below:

Alcohol extract	...	1·66% (calculated on delignified jute).
Water extract	...	3·79% ,, ,, ,,
Alkali extract	...	1·79% ,, ,, ,,

It is interesting to note that on decarboxylation of uronic acids, which may easily take place in plants by the action of enzymes, pentoses are formed according to the reaction,

$$C_6H_{10}O_7 = C_5H_{10}O_5 + CO_2.$$

Xylose would thus be formed from glycuronic acid and arabinose from galacturonic acid. These acids may therefore play an important part in the formation of pentoses and perhaps also of lignone in plants (Ehrlich, *Chem.-Ztg.*, 1917, **41**, 197).

The furfural yield of jute has so far been interpreted to indicate its pentosan content, though some investigators (Schwalbe, *Z. angew.*

Chem., 1918, **31**, 51; Hägglund and Klingstedt, *Cellulosechem.*, 1924, **5**, 58) have doubted that pentosans alone are responsible for the whole of furfural yield. In a recent paper (*Ber.*, 1925, **58**, 1534), Schwalbe has shown that a small fraction of the furfural yield of straw is due to glycuronic acid. It is evident that in the case of jute also, an appreciable fraction of the furfural yield must be attributed to uronic acids. If the furfural yield of uronic anhydride is taken as 16·6% (Norman, *Biochem. J.*, 1929, **23**, 525), 1·22% of the furfural content of jute fibre (uronic acids 8·08%) must be due to the presence of uronic acids. As the furfural content of jute has been found to be 10·06%, about 1/8th of this figure is to be attributed to uronic acids and the rest to pentosans.

Pentoses.—Arabinose and xylose have been identified by usual colorimetric tests as well as by the preparation of suitable derivatives. It will be apparent from the remarks made above, that the present method of determining pentoses from the furfural content is inaccurate and should always be supplemented by a determination of uronic carbon dioxide. From the difference of the total furfural content and that due to uronic acids, the pentosan content can be calculated. As has already been noted, the pentoses may have been formed in nature by decarboxylation of uronic acids.

Pectin.—The high uronic acid content of jute is rather significant and may indicate the presence of pectic substances, as galacturonic acid has been found by Ehrlich (*loc. cit.*) to be the main constituent of pectin. On a search being made, pectins have actually been found in appreciable amounts in jute and have been estimated as insoluble calcium salt after extraction with three different solvents, *i.e.* (1) water, (2) 0·5% oxalic acid, and (3) 0·5% ammonium oxalate solution.

The methods available for the estimation of pectin are however empirical in nature. From the wide difference between the uronic acid content (8·08%) and the pectin content (1·47%) as determined by calcium salt method, it would appear that the total amount of pectin is not obtained as insoluble calcium salt. It may be noted that the calcium-magnesium salt of pectic acid as isolated by Ehrlich (*loc. cit.*) is soluble in water. In the course of these investigations it was found that the water extract of jute, after separation of insoluble calcium pectate, had a methoxyl value of which, as in the case of pectin, 50% was in the form of ether linkage and 50% of ester linkage. Thus both the methoxyl and the carbon dioxide

values indicate that insoluble calcium salt cannot be a quantitative measure of pectin, unless pectin is defined in a special sense.

It has been found that pectins and hemicelluloses of jute may be removed almost completely by treatment with water in an autoclave at 2—3 atmos. for a period of four hours. The residual cellulose is similar in property to α-cellulose and found to be completely free from uronic carbon dioxide, the furfural content being as low as 1·58%. This figure compares satisfactorily with furfural content of α-cellulose in jute, 1·08% found by Chowdhury and Mazumdar (*loc. cit.*) and 2·4% found by Lehne and Scheppmann (*Z. angew. Chem.*, 1925, **38**, 93).

Finally it is interesting to note that when the alkali extract of delignified jute fibre is neutralised with acetic acid, no precipitate is obtained. If any water-insoluble hexosans or pentosans were present in jute, these would be extracted by alkali though not likely to be hydrolysed by it, and on neutralisation, should form a precipitate. The absence of any water-insoluble hexopentosans suggests that they are either present in jute in comparatively low molecular weights so as to be highly soluble or that they are in chemical combination with the uronic or pectic acids in which form they are soluble in water.

Experimental.

The middle portion of the fibre was taken, rejecting one foot from below and above. The fibres were then loosened by mechanical means and washed with Pear's soap to remove dust and adhering oils and fats, dried and cut into small pieces.

Jute, cut into small pieces, was extracted with chloroform to remove resin and fat. It was then subjected to the action of chlorine peroxide gas in a glass tower or a series of glass towers, until the fibre was perfectly white. The results of analysis of the original and the delignified jute are given below:

	Raw jute.	*Delignified jute.*	
α-Cellulose ...	67·25%	67·25%	(calculated on raw jute).
Lignin ...	16·21%	nil.	
Furfural ...	10·06%	10·31%	„ „ „
Resin and fat ...	1·13%	—	
Ash ...	0·501%	—	
Moisture ...	15·55%	—	
Uronic acids ...	8·08%	10·36%	„ „ „

Fractional Extraction of Hemicelluloses from Delignified Jute.

1. *Benzene Extraction.*—Delignified jute was first extracted with benzene in a Soxhlet for ten or twelve hours. On evaporating the colourless extract, a viscous oily product of characteristic woody odour was obtained. Yield—0·51%. The product was evidently resinous in nature but, owing to the small yield, was not further investigated.

2. *Alcohol Extraction.*—The fibre was then extracted with 95% alcohol. A brown mass was obtained on evaporation of the extract under reduced pressure and was found to be very similar to pectin. Yield—2·52%.

3. *Water Extraction.*—The fibre was next extracted twice with boiling water under reflux. The extract was filtered through cloth, concentrated to a syrup over a small flame and poured in a large amount of 95% alcohol when a sticky mass was obtained. This was allowed to settle, decanted and on washing with absolute alcohol and ether, was obtained as a dry amorphous powder. The yield of this alcohol-insoluble product from the first extraction was 12·66% and from the second extraction 4·35%. That these extracts consists very largely of pentoses is indicated by the high furfural value, the former giving 34·56% and the latter 30·12% furfural.

It may however be noted that a portion of the water extract, when poured in alcohol, remained in alcoholic solution and was obtained as a brown product on evaporation. The yield of this alcohol soluble product from the first extract was 5·3% (furfural, 15·88%) and from the second extract 0·72%.

4. *Alkali Extraction.*—The above extractions were followed by a treatment of the residual jute with 17·5% caustic soda. The brown extract was acidified with acetic acid and added to an excess of 95% alcohol. The white precipitate thus obtained was washed with alcohol and ether, and dried in the usual manner at a low temperature. Yield 8·6% (furfural 28·12%). Pentosans are therefore an important constituent of this extract though a part of the furfural must be attributed to uronic acids which, as estimated from carbon dioxide value, amounted to 20·09%.

As in the case of water extract, a portion of the alkali extract also remained in alcoholic solution which amounted to 6·32%.

Examination of Different Extracts.

The solid alcohol-insoluble substances obtained from water and alkali extracts were hydrolysed by treatment with 2·5% sulphuric acid for 11-12 hours on water-bath, and the acid then removed with barium carbonate. The brownish filtrate was concentrated under reduced pressure to a syrup which was then examined for different carbohydrates and acids in the manner described below. When testing for mannose, hydrochloric acid (*d* 1·025) was used instead of sulphuric acid to hydrolyse the substance.

Tests for Identification of Carbohydrates.

Galactose.—(*a*) Phenylhydrazone, recrystallised from dilute alcohol, melted at 159-160°.

(*b*) A portion of the syrup was evaporated to dryness under reduced pressure and extracted with 80% alcohol which dissolved galactose but not barium galacturonate. Alcohol was then evaporated ofi and the resulting syrup oxidised with nitric acid of sp. gr. 1·15 at 85°. Mucic acid was thus obtained which, recrystallised from hot water, melted at 213° with decomposition. As mucic acid is formed also by the oxidation of galacturonic acid, its previous separation is necessary. Galactose was identified both in water and alkali extracts.

Fructose.—(*a*) A reagent consisting of cupric hydrate, glycocoll, and potassium carbonate solutions was reduced at 15—20° in eight hours. Sugars other than fructose reduce this reagent only above 40°. This was verified by artificial mixtures of different sugars prepared in the laboratory.

(*b*) Pinoff's test which is a specific reaction for ketoses indicated the presence of fructose. This was also verified by artificial mixture of sugars.

(*c*) To a small quantity of the syrup, 3 to 5 drops of 2*N*-potassium hydroxide were added followed by 0·5−1 g. of solid caustic potash when a red band round the solid alkali was obtained (Ekkert, *Pharm. Zentr.* 1928, **69**, 805).

(*d*) α-Methylphenylhydrazone, recrystallised from dilute alcohol, melted at 158-159°.

Fructose was found mainly in the alkali extract.

Glucose.—(*a*) Barfoed's reagent, which serves as a delicate test for glucose, indicated its presence.

(*b*) The presence of glucose was also confirmed by oxidation to saccharic acid. This was possible as mannose was found absent when tested by Schorger's method.

Xylose.—The syrup was evaporated to dryness in vacuum and extracted with absolute alcohol, the extract being tested for xylose. It was found largely in the alkali extract.

(*a*) Phenylosazone, recrystallised from dilute alcohol, melted at 159-160°.

(*b*) Characteristic prismatic needles were obtained by Bertrand and Tollen's test.

(*c*) *p*-Nitrophenylhydrazone, recrystallised from alcohol, melted at 154-155°.

Arabinose.—(*a*) *p*-Bromophenylhydrazone, recrystallised from absolute alcohol, melted at 158-160°.

(*b*) Diphenylhydrazone of arabinose was also prepared.

Galacturonic acid.—This acid was found both in water and alkali extracts. Its presence was indicated by the following tests.

(*a*) The syrup gave a soluble barium salt.

(*b*) The calcium salt was obtained as microscopic prisms.

(*c*) The cadmium salt formed needles slightly soluble in water.

Estimation of Carbohydrates.

Galactose.—For the estimation of this sugar, it was freed from galacturonic acid whose barium salt was insoluble in alcohol. It was then oxidised to mucic acid by nitric acid (*d* 1·15) at 85°. The mucic acid was weighed and galactose calculated from Van der Haar's table. It was found that the water extract contained 14·12% and the alkali extract 1·78% galactose.

Fructose.—Fructose was estimated by Willstätter and Schüdell's method (*loc. cit.*) which consists in the oxidation of aldoses by means of iodine in alkaline solution leaving the ketoses unaffected.

Total reducing sugars	...	...	...	**64·27%**
Total aldoses	...	...	...	**57·87%**
Fructose (difference)	...	...	...	**6·40%**

Galacturonic Acid.—This acid was estimated from the amount of carbon dioxide evolved by treatment with 12% hydrochloric acid. The carbon dioxide was led into a standard baryta solution, the excess of which was titrated in the usual manner. The uronic acid was calculated from the following equation:

$$C_6H_{10}O_7 = C_5H_{10}O_5 + CO_2.$$

It was found that the syrup obtained from water extract had 29·92% and that from alkali extract had 20·09% uronic acids. A control experiment was made with unhydrolysed water extract which was found to contain 32·84% uronic acids. A portion of these acids was evidently destroyed by 2·5% sulphuric acid used for the purpose of hydrolysis.

Pectic Substances in Jute.

Pectic matters of delignified jute were extracted by treatment with (*a*) water, (*b*) 0·5% oxalic acid solution, and (*c*) 0·5% ammonium oxalate solution at 85° for twenty-four hours at a stretch. It was found that intermittent extraction with oxalic acid hydrolysed pectic matters. The extracts were concentrated over a small flame and poured in a large amount of alcohol, the oxalic acid extract being neutralised with ammonia before concentration. In the case of ammonium oxalate and oxalic acid extracts, alcohol acidified with hydrochloric acid was used. The precipitates were filtered and washed with acidified alcohol until free from oxalic acid, washed again with absolute alcohol and ether and dried. The actual pectin content of these alcohol insoluble extracts was then determined by the calcium pectate method of Carré and Haynes (*Biochem. J.*, 1922, **16**, 60). It may be noted that the alcoholic extract of delignified jute was also found to contain pectic substances. The following table gives the quantities of pectin, estimated by the calcium pectate method, in different extracts and also its other characteristics.

	Cal. pectate (calc. on delig. jute).	Methoxyl.	Furfural.	Uronic acids.
Alcohol extract ...	0·68%	7·15%	7·36%	30·22%
Water extract (85°) ...	1·10%	14·51%	36·91%	38·64%
Oxalic acid extract ...	1·67%	5·0%	18·61%	34·36%
Amm. oxalate extract ...	1·65%	6·87%	24·16%	37·88%

Examination of Water and Alkali Extracts freed from Pectin.

Pectin was removed from the extracts as insoluble calcium pectate by the addition of lime water. The filtrate was neutralised with acetic acid, concentrated and poured in a large amount of alcohol. In the case of alkali extract, it was neutralised with acetic acid before addition of lime water and the pectin-free substances were purified by repeated precipitation with alcohol. It was found that the water extract, when freed from insoluble calcium pectate, had a total methoxyl value of 12·2%, of which, half (6·0%) was easily removed by hydrolysis at ordinary temperature with 0·4*N*-caustic soda and was evidently in the form of ester linkage, the rest of the methoxyl (6·2%) being present as ether linkage. It would thus appear that if methoxyl number be an indication of the presence of pectin, the whole of it was not precipitated as insoluble calcium pectate. The alkali extract, freed from calcium pectate, gave 4·3% methoxyl, of which none was removed by hydrolysis with dilute alkali, the ester linkage being evidently absent in this instance.

Removal of Pectin and Hemicelluloses by Water at High Temperature.

A quantity of delignified jute after extraction with alcohol and water, was treated with water in an autoclave at three atmospheres for five hours. After removing the brown extract, the fibre was washed and dried. It was found to be practically free from any carbon-dioxide-yielding constituent while the furfural content was only 1·58%. The sample was evidently free from uronic acids and pectic substances responsible for carbon dioxide or from hemicelluloses yielding furfural.

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Heterocyclic Compounds derived from 9-Amino-10-hydroxyphenanthrene.

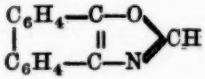
By Satish Chandra De and Tejendra Nath Ghosh.

That *o*-aminophenol forms the basis of syntheses of a number of heterocyclic compounds is well known. The object of the present investigation was to see if 9-amino-10-hydroxyphenanthrene which, like *o*-aminophenol, has the hydroxy and amino-groups in *ortho*-position to each other could similarly be utilised for the formation of heterocyclic ring systems. With this object in view, the above phenanthrene derivative was condensed with various substances such as formic and acetic acids, benzamidine hydrochloride, *o*-phenylene diamine, toluylene diamine, 1:2-naphthylene diamine, benzaldehyde and alcoholic ammonia and the condensation products derived therefrom examined. The nature of the condensation product obtained in each case has been described in the experimental portion.

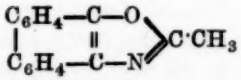
Experimental.

9-Amino-10-hydroxyphenanthrene hydrochloride required for the purpose was prepared according to the method of Schmidt (*Ber.*, 1902, **35**, 3130).

Condensation with Formic Acid: Formation of Phenanthroxazole.

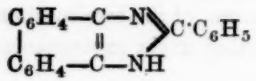


9-Amino-10-hydroxyphenanthrene hydrochloride (1 g.) was heated under reflux with an excess of formic acid for 3 to 4 hours when a brown precipitate was obtained. The precipitate was filtered from the solution and repeatedly washed with water. The residue was found to be insoluble in most solvents. So it was boiled several times with alcohol and the residue (m.p. above 300°) which was of brown colour and micro-crystalline structure was analysed. (Found: N, 6·57. $C_{15}H_9ON$ requires N, 6·39 per cent.).

N-*Methylphenanthroxazole.* 

9-Amino-10-hydroxyphenanthrene hydrochloride (1 g.) was heated under reflux with an excess of glacial acetic acid for 2 to 3 hours when a brick-red precipitate was obtained. It could not be further crystallised as it was found to be insoluble in almost all solvents. It was, therefore, successively washed several times with acetic acid and alcohol. So obtained it forms a brown crystalline powder, m.p. above 300°. (Found: C, 82·21; H, 4·93; N, 6·18. $C_{16}H_{11}ON$ requires C, 82·40 ; H, 4·72; N,6·01; per cent.). This compound is quite different from those obtained by Pschorr (*Ber.*, 1902, **35**, 2787) and Schmidt (*Ber.*, 1902, **35**, 3130) who from 9-amino-10-hydroxyphenanthrene hydrochloride and acetic anhydride obtained two different acetyl derivatives.

9-Amino-10-hydroxyphenanthrene Hydrochloride and Benzamidine Hydrochloride: Formation of N-Phenylphenanthriminazole.



The hydrochlorides of the two bases were thoroughly mixed together in molecular proportion and the mixture was heated in an oil-bath at 190-200° for about 4 hours. The mixture first melted and at the end of the reaction, solidified to a crystalline mass which was detached from the tube, finely powdered and then treated with boiling water. The residue was repeatedly boiled with alcohol and acetic acid and finally crystallised from a mixture of pyridine and water; m.p. above 300°. (Found: C, 85·85; H, 4·88; N, 9·75. $C_{21}H_{14}N_2$ requires C, 85·71; H, 4·76; N, 9·52 per cent.).

9-Amino-10-hydroxyphenanthrene Hydrochloride and o-Phenylene Diamine: Formation of Phenanthraphenazine.

A finely powdered mixture of *o*-phenylene diamine (1 g.), 9-amino-10-hydroxyphenanthrene hydrochloride (2·5 g.) and fused zinc chloride (1 g.) was heated in a boiling tube in an oil-bath for about 4 hours at 175-180°. There was at first formed a molten semi-solid mass which ultimately formed into a soild cake. The soild melt was detached from the tube, finely powdered and boiled several times with water. It was next washed with acetic acid and was finally

crystallised from acetone in light yellow crystals, m.p. 217°. (Found: C, 85·58; H, 4·48; N, 10·14. $C_{20}H_{12}N_2$ requires C, 85·71; H, 4·28 N, 10·00; per cent.).

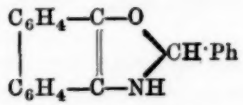
9-Amino-10-hydroxyphenanthrene Hydrochloride and 1:3:4-Toluylene Diamine: Formation of N-Methylbenzophenanthrazine or Phenanthratolazine.

It was similarly prepared, the temperature being 190-95°. The solid cake so obtained was finely powdered, boiled several times with water and acetic acid and then crystallised from acetone; m.p. above 212°. (Found: N, 9·68. $C_{21}H_{14}N_2$ requires N, 9·52 per cent.).

9-Amino-10-hydroxyphenanthrene Hydrochloride and 1:2-Naphthalene Diamine: Formation of Naphthophenanthrazine or Phenanthranaphthazine.

The condensation was carried out at 200°. The solid cake was boiled with acetic acid and alcohol and then crystallised from acetone; m.p. above 273°. (Found: N, 8·61. $C_{24}H_{14}N_2$ requires N, 8·48 per cent.).

9-Amino-10-hydroxyphenanthrene Hydrochloride and Benzaldehyde Formation of N-Phenyldihydrophenanthroxazole.



The reactants (1 mol. each) were warmed together in alcohol in a current of hydrochloric acid gas. After about an hour the reddish-brown crystalline mass that was formed was successively washed with hot water, acetone, acetic acid and alcohol. It could not be crystallised from any solvent; m.p. above 300°. It is insoluble in alkalis. (Found: C, 85·09; N, 4·85; H, 5·26. $C_{21}H_{15}ON$ requires C, 84·84; H, 5·05; N, 4·71 per cent.).

Phenanthroxazine.—This compound was obtained by heating 9-amino-10-hydroxphenanthrene hydrochloride in a sealed tube at 230-240° for 5 to 6 hours. The fused mass was powdered and repeatedly boiled with alcohol and the residue was then treated with dilute ammonia. The brownish-red product so obtained, was then

crystallised from nitrobenzene in which it is fairly soluble. It forms green needles with a bright coppery lustre, m.p. above 300°. (Found: N,3·85. $C_{28}H_{17}ON$ requires N,3·65 per cent.). This compound is identical with that prepared by Bamberger and Grob (*Ber.*, 1901, **34**, 535).

Phenanthrazine.—When 9-amino-10-hydroxyphenanthrene hydrochloride was heated in a sealed tube with alcoholic ammonia at 150-160° for 4—5 hours it was converted into phenanthrazine. The reaction product was filtered from alcohol and the dirty brown residue was successively boiled with alcohol and acetic acid and finally extracted with boiling nitrobenzene from which on cooling a yellow micro-crystalline powder was obtained; m.p. above 300°. (Found: N, 7·52. $C_{28}H_{16}N_2$ requires N, 7·37 per cent.). It is identical with the compound obtained by Bamberger and Grob (*loc. cit.*).

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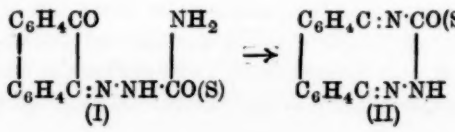
Action of Hydrazides. Part III. Condensation of Semi- and Thiosemi-carbazide with Phenanthraquinone and its Derivatives and the Synthesis of Triazines.

By Satish Chandra De.

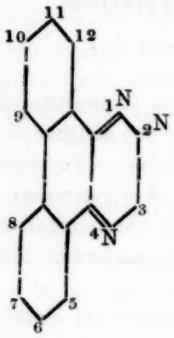
The three substances semicarbazide, thiosemicarbazide and aminoguanidine are so closely related to one another in structure that they might be expected to give similar products when condensed with one and the same substance; but nevertheless, there is a distinct difference between the action of thiosemicarbazide and semicarbazide on the one hand and aminoguanidine on the other towards 1:2-diketones.

It is well known that while semicarbazide reacts with 1:2-diketones, excepting benzil, to form semicarbazones, the triazines are the sole products of the action of aminoguanidine on phenanthraquinone and other aromatic diketones (*J. Indian Chem. Soc.*, 1927, **4**, 183). The behaviour of thiosemicarbazide towards 1:2-diketones appears not to have been investigated in most cases and to my knowledge the only evidence found in literature is that of the action of the hydrazide on benzil, the product being 3-thiol-5:6-diphenyl-1:2:4-trizine.

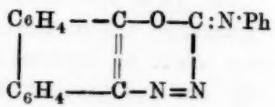
It has now been possible to show that thiosemicarbazide behaves exactly like semicarbazide towards phenanthraquinone and its derivatives in giving thiosemicarbazones whilst with the monoximes of the diketone and its derivatives it gives triazines. It has also been possible to convert the thiosemicarbazones and semicarbazones of phenanthraquinone and its substitution products into triazines, a reaction which appears not to have been pointed out by any of the previous investigators. The formation of triazines from the thiosemicarbazones or semicarbazones probably takes place in the following way:



Though theoretically the formation of two isomeric triazines is possible from monosubstituted phenanthraquinones (depending on whether the keto-group in position 9 or 10 should first react to form the thiosemicarbazones) only one triazine is actually formed in every case. The following system of numbering the positions in the phenanthratriazines has been adopted:



(III)



(IV)

During the conversion of the thiosemicarbazones of phenanthraquinone and its derivatives into triazines a very slow evolution of hydrogen sulphide was noticed but no sulphur-free compound, as the product of a probable side-reaction, could be isolated. When, however, the 4-phenylthiosemicarbazone of phenanthraquinone was boiled in acetic acid for a long time copious hydrogen sulphide was evolved and a dark coloured solid free from sulphur was obtained. This substance contains an abnormally low percentage of nitrogen than what is demanded by the expected formula (IV).

The exact nature of the reaction as also similar other abnormal reactions which are being studied in other cases will be communicated in a subsequent paper.

Experimental.

Phenanthraquinone thiosemicarbazone.—It was prepared from phenanthraquinone and thiosemicarbazide in acetic acid solution, and crystallised from acetic acid in yellow needles, m. p. 212°. (Found: N, 14·82. $C_{15}H_{11}ON_3S$ requires N, 14·94 per cent.).

3-Thiolphenanthratriazine.—The above thiosemicarbazone was

heated in acetic acid solution for 30 hours, the solution gradually darkening in colour. During heating there was also noticed a slight evolution of hydrogen sulphide. The reaction mixture was filtered hot and the residue was crystallised from pyridine in dull red rectangles, m. p. 198°. Inspite of repeated searches no sulphur-free compound could be obtained. The same compound was also obtained from phenanthraquinone monoxime and thiosemicarbazide. The mixture was heated for 5 to 6 hours during which a dark coloured precipitate gradually separated which after being boiled with acetic acid was crystallised from pyridine. It is insoluble in acetic acid, alcohol and benzene but readily soluble in pyridine and nitrobenzene. (Found: N, 16·10. $C_{15}H_9N_3S$ requires N, 15·97 per cent.).

2-*Nitrophenanthraquinone thiosemicarbazone* was prepared as before from 2-nitrophenanthraquinone and crystallised from pyridine in red rectangles, m. p. 234-235°. It is insoluble in alcohol and benzene; slightly soluble in acetic acid but readily so in hot pyridine. (Found: N, 17·31. $C_{15}H_{10}O_3N_4S$ requires N, 17·18 per cent.).

3-*Thiol*-6-*nitrophenanthrotriazine*.—The above thiosemicarbazone was heated in acetic acid suspension for 35 hours when the deep red colour became dirty red. The solid was separated, boiled with pyridine to remove any unchanged thiosemicarbazone. The residue could not be crystallised from the ordinary organic solvents. The same compound was obtained by heating for 8 to 10 hours a mixture of 2-nitrophenanthraquinonemonoxime and thiosemicarbazide ; m. p. above 300°. It dissolves in nitrobenzene from which, however, it does not separate. (Found: N, 18·00. $C_{15}H_8O_2N_4S$ requires N, 18·18 per cent.).

2:7-*Dinitrophenanthraquinone thiosemicarbazone* was prepared as before from 2:7-dinitrophenanthraquinone. From the clear solution a red precipitate separated. This was recrystallised from the minimum quantity of acetic acid in brown rectangles, m. p. 258°. (Found: N, 19·00. $C_{15}H_9O_5N_5S$ requires N, 18·87 per cent.).

3-*Thiol*-6:11-*dinitrophenanthratriazine*.—The above thiosemicarbazone was heated in acetic acid solution for 20 hours. As the reaction proceeded a brown solid separated. This was filtered hot and the residue, after being boiled with acetic acid, was crystallised from pyridine in brown rectangles, m. p. 220°. The same compound was also obtained by heating an acetic acid solution of 2:7-dinitrophenanthraquinone monoxime and thiosemicarbazide for 4 hours. It is insoluble in alcohol, benzene and acetic acid but readily soluble in hot

pyridine. (Found: N, 19·72. $C_{15}H_7O_4N_5S$ requires N, 19·83 per cent.).

4-*Nitrophenanthraquinone thiosemicarbazone* was prepared as before from 4-nitrophenanthraquinone. The clear acetic acid solution obtained was diluted with water when a reddish-brown solid was precipitated. This was crystallised from a mixture of pyridine and alcohol; m. p. 145°. (Found: N, 17·00. $C_{15}H_{10}O_3N_4S$ requires N, 17·18 per cent.)

3-*Thiol*-8-*nitrophenanthratriazine*.—A solution of 4-nitrophenanthraquinone monoxime and thiosemicarbazide hydrochloride was heated for 6 to 7 hours. The solid that separated was filtered hot, boiled with acetic acid and crystallised from pyridine in brown rectangles; m. p. 230°. It is insoluble in acetic acid and alcohol but easily soluble in pyridine. (Found: N, 18·39. $C_{15}H_8O_2N_4S$ requires N, 18·18 per cent.).

3-*Hydroxyphenanthrotriazine*.—Phenanthraquinone semicarbazone was heated in acetic acid solution for 15 to 16 hours. The solid product obtained was filtered and crystallised from alcohol; m. p. 287°. (Found: N, 17·21. $C_{15}H_9ON_3$ requires N, 17·00 per cent.)

8-*Nitro*-3-*hydroxyphenanthrotriazine*.—4-Nitrophenanthraquinone-semicarbazone was heated as before in acetic acid solution for 25 hours. The solid product was crystallised from alcohol ; m. p. 286°. (Found: N, 19·39. $C_{15}H_8O_3N_4$ requires N, 19·19 per cent.).

2:7-*Dibromophenanthraquinone semicarbazone* was prepared from 2:7-dibromophenanthraquinone and semicarbazide hydrochloride in yellow needles, m. p. above 300°. (Found: N, 10·04. $C_{15}H_9O_2N_3Br_2$ requires N, 9·93 per cent.).

6:11-*Dibromo*-3-*hydroxyphenanthratriazine*.—The above semicarbazone was suspended in acetic acid and heated for 10 hours when it gradually went into solution from which a light yellow crystalline mass separated. This was crystallised from alcohol in yellow rectangles, m. p. 295°. (Found: N, 10·52. $C_{15}H_7ON_3Br_2$ requires N, 10·37 per cent.).

Phenanthraquinone phenylthiosemicarbazone was obtained from phenanthraquinone and 4-phenylthiosemicarbazide as a red crystalline precipitate. This crystallised from pyridine in orange-red needles, m. p. 206°. (Found: N, 11·85. $C_{21}H_{15}ON_3S$ requires N, 11·76 per cent.).

When the above thiosemicarbazone was heated for about 30 hours in acetic acid suspension copious hydrogen sulphide was evolved

and the thiosemicarbazone gradually went into solution and at the same time a dark coloured solid separated. This was filtered hot, boiled with acetic acid and the residue crystallised from nitrobenzene in dark plates with a green lustre, m. p. above 300°. With the exception of nitrobenzene, it is insoluble in all other ordinary organic solvents. An analysis of the compound shows that it contains 4·93 per cent. of nitrogen.

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Preparation of Borate, Tungstate, Molybdate and other Jellies and Study of Mercurisulphosalicylic Acid Jellies.

By Satya Prakash and N. R. Dhar.

In previous communications from these laboratories (*Z. anorg. Chem.*, 1927, **168**, 214; *J. Indian Chem. Soc.*, 1929, **6**, 587) we have investigated the conditions of formation of various hydroxide, arsenate, phosphate, molybdate, tungstate and borate jellies and have also studied the changes in viscosity and hydrogen ion concentrations during the process of their gelation (*J. Indian Chem. Soc.*, 1929, **6**, 391). In this paper, we are recording the methods of preparation of the following jellies which have been obtained by us for the first time:

1. Chromic tungstate.
2. Ferric tungstate.
3. Zirconium molybdate.
4. Zirconium borate.
5. Ceric arsenate.
6. Ceric borate.

Our results with the jellies of mercurisulphosalicylic acid and its sodium salts are also recorded in this paper.

Chromic Tungstate Jellies.

It appears that chromium salts have less tendency to form jellies when compared with iron salts. An attempt to prepare molybdate or borate jellies has so far been unsuccessful and the only jellies of chromium salts that have been obtained are chromium arsenate and phosphate.

When sodium tungstate solution is added to chromic chloride solution, a bulky greenish-white precipitate is formed, which slightly dissolves on shaking at the room temperature (25-30°) even when chromic chloride is present in large excess. However if the mixture is warmed and shaken, a sufficient amount of chromic tungstate is peptised and it forms a clear transparent solution. If this solution is now allowed to dialyse for about ten days, a translucent sol is

obtained which sets to a jelly on addition of potassium sulphate. To *M*/1·5-chromic chloride solution, a 15 per cent. solution of sodium tungstate was added and the mixture was warmed and shaken. The amount of sodium tungstate was added so long as the precipitate formed could be redissolved on warming. The solution still contained much of the free chromic chloride, and it was dialysed for ten days, when a translucent sol was obtained. This sol sets to a jelly when kept in a Jena bottle for about a month. The sol gives jellies readily on adding potassium sulphate.

Concentration of the sol = 23·86 g. chromic tungstate per litre.

Amount of sol taken each time = 2 c.c.

Total volume was made 3 c.c. or 6 c.c. each time by adding the requisite amount of water.

TABLE I.

Potassium sulphate.	Total volume.	Observations.
N/20—1·0 c.c.	3 c.c.	Gelatinous precipitate.
0·5	3	Gelatinous precipitate.
0·3	3	Sets to green, opaque, loose jelly in 30 minutes, soon synerises.
0·1	3	Sets to firm opalescent jelly within 24 hours; syneresis not marked.
N/50—0·5	3	Sets in 1 hour 45 minutes to opaque, loose jelly, which synerises soon.
0·4	3	Sets in 25 hours to firm jelly with slight syneresis.
0·3	3	Sets in 24 hours with no syneresis.
0·2	3	Sets in 2 days with no syneresis
0·5	6	Sets in 24 hours; no syneresis.
0·4	6	Sets in 24 hours; no syneresis.
0·3	6	Sets to translucent jelly in 24 hours.
0·2	6	Sets in 2 days to firm translucent jelly.

Ferric Tungstate Jelly.

In a previous paper (*loc. cit.*), we have shown that when suitable concentrations of sodium tungstate are added to ferric chloride solution in excess, the mixture sets to a yellow opaque jelly. We have now observed that more transparent jellies are obtained when a mixture of sodium tungstate and ferric chloride taken in excess is

dialysed and the sol thus obtained is coagulated with electrolytes. To 75 c.c. of 0·929*M*-ferric chloride solution was added a solution of 16·5 g. sodium tungstate (Na_2WO_4, $2H_2O$) with vigorous shaking and slight warming, and the volume was made up to a litre. The mixture was filtered and dialysed for 6 days. The clear sol so obtained sets to translucent jellies on the addition of suitable amounts of electrolytes.

Concentration of the sol = 21·68 g. ferric tungstate per litre.
Amount of sol taken each time = 4 c.c.
Total volume = 5 c.c.

TABLE II.

Electrolyte.	Observations.
N-*Potassium chloride.*	
0·2 c.c.	Translucent jelly in 1 day ; syneresis starts after 3 days.
0·4	,, ,, ,,
0·6	Loose jelly in 2 hours.
0·8	Loose opaque jelly in 45 mins.
1·0	No jelly ; coagulated gelatinous mass.
N/20-*Potassium sulphate.*	
0·2 c.c.	Sets in 1 day to a translucent jelly.
0·4	,, ,, ,,
0·5	Sets in 6 minutes to a jelly.
0·6	Sets to a jelly in 2 mins.
0·8	Sets to a jelly in 1 min.

Most of the tungstate jellies prepared are loose and translucent with slight opalescence and have marked tendency towards syneresis.

Zirconium Molybdate Jellies.

No arsenate or phosphate jellies of zirconium have yet been reported. When potassium arsenate or phosphate is added to a solution of zirconium nitrate, a white gelatinous precipitate is formed which can be peptised only slightly by adding excess of zirconium nitrate. For this reason, it is not possible to obtain a sol of either zirconium arsenate or phosphate of suitable concentrations. Only bulky white opaque jellies of arsenate or phosphate are sometimes

obtained, when the mixture of potassium arsenate or phosphate and zirconium nitrate is warmed up to 90°. No jellies of fine texture have yet been obtained.

When potassium molybdate solution is added to zirconium nitrate solution, a white precipitate of zirconium molybdate is obtained, which is easily dissolved by an excess of zirconium nitrate on shaking. In this way, a sufficient amount of zirconium molybdate can be peptised, and a concentrated sol could be obtained. This sol on dialysis gives suitable jellies when coagulated with electrolytes. If the sol is dialysed for a long time, it either sets on the parchment paper or gives a transparent jelly on standing for some days without the addition of electrolytes. Some of the jellies prepared by the coagulation of the sol by potassium chloride, develop opalescence, and may even become opaque.

To 70 c.c. of $M/1{\cdot}33$-zirconium nitrate solution was added a 10 per cent. solution of potassium molybdate, till the precipitate obtained just dissolved in the excess of zirconium nitrate. The total volume of the mixture was made 200 c.c. and the sol thus obtained was dialysed for 36 hours. Strength of the sol = 50·38 g. zirconium molybdate per litre.

TABLE III.

Total volume = 4 c.c.

Zirconium molybdate sol.	Electrolyte.	Observations.
	N-KCl	
2 c.c.	0·3 c.c.	Sets to a transparent jelly in 3 hours.
2	0·4	Sets to a transparent jelly in 30 minutes.
2	0·6	Sets to an opalescent jelly in 20 minutes.
3	0·2	Clear solution, no jelly.
3	0·3	Sets to a transparent jelly in 90 minutes.
3	0·4	Sets to an opalescent jelly in 6 minutes.
3	0·6	Opalescent jelly in 2 mins.
3	0·8	,, ,, ,, 1 min.
3	1·0	Immediately set to an opaque jelly.
	$N/5$-K_2SO_4	
2	0·2	Clear solution, no jelly.
2	0·3	Translucent jelly in 2½ hrs.
2	0·4	,, ,, 6 mins.
2	0·5	,, ,, immediately; slight syneresis observed.
3	0·1	Transparent jelly in 3½ hrs.
3	0·3	,, ,, 2 hrs.
3	0·4	,, ,, 30 mins.
3	0·5	Opalescent jelly in 12 mins.

Zirconium Borate Jellies.

Zirconium borate jellies have been prepared in the same way as molybdate jellies. A hot concentrated solution of borax was added to 70 c.c. of $M/1{\cdot}33$-zirconium nitrate solution till the precipitate of zirconium borate obtained just dissolved in the excess of zirconium nitrate. The total volume of the solution was made 200 c.c. and allowed to dialyse for 3 days.

Concentration of the sol = 34·62 *g.* zirconium borate per litre.

This sol gives transparent or opalescent jellies when coagulated by electrolytes.

TABLE IV.

Total volume = 4 c.c.

Zirconium borate sol.	Electrolytes.	Observations.
	N-KCl	
2 c.c.	0·2 c.c.	Opalescent jelly in 1 day.
2	0·4	Transparent jelly in 7 minutes, which develops opalescence soon.
2	0·5	Translucent jelly in 3 minutes.
2	0·7	Opalescent jelly in 1 minute.
2	0·9	Immediately sets to an opaque jelly.
3	0·1	No jelly.
3	0·3	Transparent jelly in 20 minutes.
3	0·5	Translucent jelly in 3 minutes.
3	0·7	Opalescent jelly in 1 minute.
3	0·9	Immediately sets to an opaque jelly.
	$N/5$-K_2SO_4	
2	0·2	Clear solution, no jelly.
2	0·3	" " "
2	0·5	Transparent jelly in 1 hour.
2	0·6	Transparent jelly in 10 minutes.
2	0·8	Translucent jelly immediately formed; syneresis starts at once.
3	0·5	Transparent jelly in 40 minutes.
3	0·4	" " "
3	0·3	Clear solution, no jelly.
3	0·2	" "

It has been observed in the case of both zirconium molybdate and borate, that the jellies are more readily obtained when sols are coagulated by potassium chloride but these jellies develop opalescence on standing. When sols are coagulated by potassium sulphate, the jellies are more transparent and do not develop marked opalescence. More syneresis is observed in the case of potassium sulphate than in the case of potassium chloride.

Ceric Arsenate Jelly.

When a solution of potassium arsenate is added to ceric ammonium nitrate solution in small quantities and allowed to stand, yellow opalescence develops after a time and under suitable concentrations the whole mass sets to a fine transparent or opaque jelly. Some of the jellies are loose and in almost all the cases, they undergo syneresis within 12—24 hours and finally break up.

To a 10 per cent. solution of ceric ammonium nitrate, various quantities of potassium arsenate (18 per cent. solution) were added, and the volume was made the same in all the cases by adding the requisite amount of water. The observations are recorded in the following table.

TABLE V.

Total volume = 4·5 c.c.

Cerric ammonium nitrate.	Potassium arsenate.	Observations.
4 c.c.	0·1 c.c.	No jelly.
4	0·15	Loose jelly in 1 hour.
4	0·2	Firm transparent jelly with opalescence in 15 minutes.
4	0·25	Translucent jelly in 3 minutes.
4	0·3	Yellow opaque jelly in 1 minute.
4	0·4	Opaque jelly in ½ minute.
3	0·3	Loose, translucent jelly in 1 minute; soon breaking.
3	0·25	,, ,, ,,
3	0·2	Loose translucent jelly in 3 mins.
3	0·15	Firm translucent jelly in 5 mins.

Ceric Borate Jellies.

When a solution of borax is added to a solution of ceric ammonium nitrate, a yellowish-white precipitate is obtained which readily dissolves on shaking, if the ceric ammonium nitrate is in excess. If the mixture of these two substances is allowed to stand for some time, the contents are generally precipitated, though in some cases, loose unstable jellies may also form.

The clear solution formed by mixing 100 c.c. of 10 per cent. ceric ammonium nitrate and 35 c.c. of 15 per cent. borax solution was dialysed for 24 hours. The sol thus obtained not only gave a jelly on treatment with potassium sulphate; but also on keeping for some time in a Jena bottle, its viscosity increases coutinuously and in the next 24 hours, it sets completely to an opalescent jelly. Another sol was prepared by mixing only 30 c.c. of 15 per cent. borax solution to ceric ammonium nitrate. The mixture on dialysis gave a clear sol in 24 hours. This sol was quite stable and could be kept for weeks and gave jellies only on the addition of potassium sulphate. The results are recorded below.

TABLE VI.

Concentration of the sol=36·44 g. ceric borate per litre.
Total volume=5 c.c.

Ceric borate sol.	Potassium sulphate.	Observations.
3 c.c.	*N*/20—1·0 c.c.	Firm translucent jelly in 24 hours.
3	1·3	Loose jelly in 24 hours.
3	1·4	Loose jelly in 2½ hours.
3	1·5	Loose jelly in 1½ hours.
3	1·6	Gelatinous precipitate.
3·5	1·5	Translucent firm jelly in 1 hour 45 mins.
4·0	*N*/5—0·4 c.c.	Firm transparent jelly in 3 hours.
4·0	0·5	Transparent jelly with opalescence in ½ hour.

Mercurisulphosalicylic Acid Jellies.

Berkmann and Zocher (*Kolloid Z.*, 1927, **42**, 309, 322) studied the anisotropy and double refraction of mercurisulphosalicylic acid sols. Wo. Ostwald and Mertens (*Kolloid Chem. Beih.* 1926, **23**, 242)

studied the colloidal properties of complex mercuri-derivatives of sulphosalicylic acid. In a previous communication (*loc. cit.*) we have studied the changes in viscosity during the process of gelation, when freshly precipitated mercuric oxide is dissolved in sulphosalicylic acid solution. There we observed that for the first six hours, there was no marked increase in the viscosity and then for the next three hours, a regular exponential increase with time was observed, and this was followed by an abrupt increase in the viscosity till the solution sets to a transparent jelly.

When freshly precipitated mercuric oxide is dissolved in sulphosalicylic acid solution, perfectly transparent jellies are obtained within 24 hours, if the concentration of mercuric oxide is regulated. These jellies are perfectly stable and do not undergo marked syneresis. With higher concentrations of mercuric oxide, opaque jellies are produced. The jellies of mercurisulphosalicylic acid are heat-reversible. On being dried on a water-bath, a white powder is obtained and this gives a viscous sol when shaken with water, and when the concentration is suitable, sets to a transparent or translucent jelly. 1·5 Mols. of mercuric oxide were dissolved in 1 mol. of sulphosalicylic acid and the mixture was dried on a water-bath. The powder of mercurisulphosalicylic acid sets to jellies when dissolved in water in proper concentrations as shown in the following table.

TABLE VII.

Total volume=5 c.c.

Mercurisulphosalicylic acid.	Observations.
0·1 g.	No jelly within 24 hours.
0·3	,, ,, ,,
0·5	Transparent jelly within 40 minutes.
0·7	Transparent jelly in 20 minutes.
0·9	Turbid jelly in 10 minutes.

Most of these jellies are transparent but they are not uniform because it becomes very difficult to get a clear homogeneous solution of mercurisulphosalicylic acid at such concentrations. Like soap jellies, the jellies of mercurisulphosalicylic acid so prepared melt on heating and again set on cooling as is shown in the following table.

TABLE VIII.

Total volume=5 c.c.

Mercurisulphosalicylic acid.	Time of setting.	Time of setting after once being melted and cooled.
0·5 g.	40 min.	15 min.
0·7	20	2
0·9	10	Instantaneous setting.

It will be seen from the above table that the time of setting of the jelly when once melted is much less than the original setting time.

The sodium salt of mercurisulphosalicylic acid is prepared by adding 1 mol. of sodium hydroxide to 1 mol. of mercurisulphosalicylic acid. If to a solution of mercurisulphosalicylic acid, the requisite amount of sodium hydroxide is added, and the mixture dried on a water-bath, a white powder is obtained. It has been observed that this white powder of sodium mercurisulphosalicylate loses its power of setting to a jelly when re-dissolved in water. In this respect it appears to be heat-irreversible and differs from the original mercurisulphosalicylic acid. All concentrations between 0·1 g. and 0·6 g. of this sodium salt in 5 c.c. total volume have been tried but no jelly could be obtained with this substance.

The jellies of the sodium salt can be obtained by adding the calculated amount of sodium hydroxide to mercurisulphosalicylic acid, when the concentration is suitable. The comparative results for the time of setting of the original acid jelly and also its sodium salt are given in the following table.

TABLE IX.

Total volume=5 c.c.

For the preparation of sodium salt, for each 0·1 g. of mercurisulphosalicylic acid, 0·116 c.c. of 2·08*N*-sodium hydroxide has been used.

Mercurisulphosalicylic acid.	Time of setting for the acid jelly.	Time of setting for the sodium salt jelly.
0·1 g.	No jelly in 24 hours.	No jelly in 24 hours.
0·3	" " "	10 min.
0·5	40 min.	8 min.
0·7	20 min.	5 min.

The results recorded in the above table show that the sodium salt more readily sets to jelly than the original acid of the same concentration. However, it has been observed that the jellies of the sodium salt are more opaque than the corresponding acid jellies. It

clearly shows that in the sodium salt the agglomeration tendency of the particles is more prominent than the hydration tendency; and this is probably the reason why, once dried, the sodium salt does not set when re-dissolved in water. The jellies of the sodium salt also melt when heated and re-set on cooling.

TABLE X.

Total volume=5 c.c.

Amount of mercurisulphosalicylic acid in salt jelly.	Time of setting of the sodium jelly.	Time of setting after once being melted and cooled.
0·3 g.	10 mins.	20 mins.
0·5	8	11
0·7	5	5

The above table shows that the time of setting of the jelly when once melted is greater than the original setting time. This also shows that in contrast to acid jellies, the hydration tendency of the sodium salt particles is much less, as was also seen from the heat irreversibility of the sodium salt jelly.

For the preparation of these acid or salt jellies, a sufficiently high concentration of mercurisulphosalicylic acid is required. But the jellies so prepared are very stable and do not exhibit marked syneresis. However, more dilute jellies can be obtained if the colloidal solution of the mercurisulphosalicylic acid is coagulated by electrolytes.

In the preparation of the following jellies 4 c.c. of 1 per cent. solution of mercurisulphosalicylic acid were used, and the total volume was made 5 c.c. in all the cases.

TABLE XI.

Electrolyte.	Observations.
N-*Potassium nitrate.*	
0·3 c.c.	Translucent jelly in 5 minutes.
0·5	Translucent jelly in 2 minutes, soon syneresing.
N-*Potassium sulphate.*	
0·2 c.c.	Translucent jelly in 1 hour.
0·3	Transparent jelly in 40 minutes.
0·4	Transparent jelly in 2 minutes.
0·6	Opalescent jelly in 1 minute.
0·8	" " "
1·0	Translucent jelly immediately—which soon undergoes syneresis.
N/10-*Barium nitrate.*	
0·2 c.c.	No jelly.
0·3	Opaque jelly in 1 minute, soon syneresing.
0·5	Opaque jelly immediately, soon syneresing.

When to the solution of mercurisulphosalicylic acid, potassium, lithium or barium chloride is added, the dissolution of the colloidal phase appears to occur and a clear solution which is less viscous than the original sol is obtained and this does not coagulate on adding concentrated solutions of potassium sulphate or barium nitrate.

The sodium salt of mercurisulphosalicylic acid yields a negatively charged sol which sets to a jelly on the addition of electrolytes. To 1 g. of mercurisulphosalicylic acid were added 1·16 c.c. of 2·08 *N*-sodium hydroxide solution, and the total volume was made up to 100 c.c. For the preparation of the jellies of this sodium mercurisulphosalicylate, 4 c.c. of the solution were taken each time, and varying quantities of potassium sulphate or barium nitrate were added ; the total volume was kept 5 c.c. in each case. The results are recorded below.

TABLE XII.

Electrolyte.	Observations.
N-*Potassium sulphate.*	
0·2 c.c.	Translucent jelly in 10 minutes.
0·3	,, ,, 6 ,,
0·4	,, ,, 3 ,,
0·6	,, ,, 3 ,,
1·0	Opaque precipitate.
N/10-*Barium nitrate.*	
0·05 c.c.	No jelly.
0·1	Translucent jelly after 24 hours.
0·2	Precipitate in 24 hours ; no jelly.
0·3	Opaque loose jelly in ½ hour, soon synerising.

Comparing the results of this table with those of the previous one on the acid jellies, it will be seen that at the same concentration of the jelly and the coagulating electrolyte, the time of setting for the acid jelly is much greater than for the sodium salt jelly. The jellies of both the acid and the salt are opalescent and undergo marked syneresis. They are not so stable as those prepared without the addition of electrolytes. The colloidal solution of sodium salt also undergoes dissolution when chloride ions are added to it.

Wo. Ostwald and Mertens (*loc. cit.*) have observed that Cl-, Br-, CN-, and CNS-ions exert " dissolving " influence on sols of mercurisulphosalicylic acid derivatives, and they assume a true chemical

combination with the formation of a compound of the type sodium 3-chloromercuri-5-sulphosalicylate when mercurisulphosalicylic acid is mixed with sodium chloride. Such examples of chlorination by the mere addition of sodium chloride are not familiar in organic chemistry. What appears to be more probable is that the addition of chloride ions displaces the mercury of sulphosalicylic acid derivatives. This view is further supported by the fact that the mercuration of sulphosalicylic acid is far easily conducted by freshly precipitated mercuric oxide free from chloride ions than by mercuric chloride. The crystalline compound, decomposing at 240° which Wo. Ostwald takes to be a chloromercuri-compound, appears to be a mixture of mercuric chloride and sodium sulphosalicylate.

Summary.

1. Jellies of chromic tungstate, ferric tungstate, zirconium molybdate, zirconium borate and ceric borate have been prepared for the first time by coagulation of the sols obtained by dialysing the mixtures of chromic chloride, ferric chloride or ceric ammonium nitrate and sodium tungstate, potassium molybdate or borax. Ceric arsenate jelly was obtained by mixing the solution of potassium arsenate and ceric ammonium nitrate.

2. The jellies of mercurisulphosalicylic acid were prepared by three methods; (*a*) by dissolving the freshly precipitated mercuric oxide in sulphosalicylic acid, which gives stable transparent jellies; (*b*) by re-dissolving the dried powder of mercurisulphosalicylic acid at high concentrations; and (*c*) by coagulating the dilute sol of mercurisulphosalicylic acid with electrolytes when translucent or opaque jellies are obtained which undergo marked syneresis.

3. The jellies of sodium mercurisulphosalicylate are heat-irreversible and it has been observed that the jelly-forming tendency of the salt is less than that of the acid.

4. The jellies of mercurisulphosalicylic acid and its salt melt when heated and re-set on cooling like soap jellies.

5. The ' dissolving influence ' of chloride ions is ascribed to the displacement of mercury from the mercurisulphosalicylic acid derivative and not to the formation of chloromercuri-derivatives as Wo. Ostwald thinks.

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Decolourisation of Oils with Mixed Adsorbents.

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Pure inorganic adsorbents such as silica gel, aluminium and ferric hydroxides etc., are characterised by inertness to many chemicals, non-inflammability and capability of easy regeneration; but they suffer from the disadvantage that their activity as decolourising agents for mineral and vegetable oils is comparatively low. Attempts have been made in the past by various investigators to improve the activity of inorganic adsorbents. Thus Patrick and others (Patrick and McGavack *J. Amer. Chem. Soc.*, 1920, **42**, 946; Munro and Johnson, *Ind. Eng. Chem.*, 1925, **17**, 88; Wood, Shelley and Trusty, *ibid.* 1926, **18**, 169) have studied the optimum conditions for the preparation of silica and other gels. Siliceous decolourisers of high activity have also been obtained by the treatment of suitable earths with inorganic acids (Koetschsau, *Z. angew. Chem.*, 1926, **39**, 210). A new principle for the preparation of suitable adsorbents has been followed by some investigators (E.P. 243123, 255904; Reyerson, *J. Phys. Chem.*, 1927, **31**, 88) who incorporated catalytic substances such as copper, nickel and platinum, etc., with silica and other inorganic gels. It is claimed that these mixed masses are highly suitable both as catalysers and as adsorbents of high activity.

In a previous paper (Chowdhury and Bagchi, *J. Indian Chem. Soc.*, 1928, **5**, 111) it has been shown that specially prepared mixed adsorbents consisting of alumina and silica gels have much higher activity for removal of sulphur compounds, than either of the constituents separately. This result has received confirmation in the work of Chowdhury and Pal (published in this issue) who have shown that silicalised bauxite has a higher adsorptive capacity for benzol vapour than either bauxite or silica alone. It is here intended to extend the above observations to the decolourisation of mineral and vegetable oils and to the preparation of suitable mixed adsorbents for the purpose. In the following investigations, pure silica gel has been prepared by the method of Patrick (*loc. cit.*), and alumina gel by the method of precipitating the gel from aluminium sulphate solution by ammonia. The principle for the preparation and activation of mixed adsorbents is the same as that followed by Chowdhury and Bagchi (*loc. cit.*), except that in a few instances the method of drying has been modified.

The decolourisation tests were carried out as follows:—100 c.c. of the oil (coloured kerosene and groundnut oils) were taken in a glass stoppered bottle and shaken mechanically with different amounts of

decolourisers (freshly dried) for different lengths of time, the colour being measured after each experiment with tintometers.

Measurement of Colour.—The Lovibond tintometer was used for the purpose. Attempts were at first made to use the Dubosque type of colorimeter, in which a known thickness of the original oil was matched with carefully measured depths of the decolourised (treated) oil. It was however found that the two columns of oil could never be satisfactorily matched. The colour of the original and the treated oils not being identical, it is evident that the original colour is not due to any single substance, but to a mixture of substances of different colours. Owing to the specific nature of all adsorbents, these coloured substances are removed to a different degree by each decolouriser, so that the treated oil gets a different shade of colour from that of the original. A satisfactory method of measuring decolourisation must, therefore, take into account the different degree of removal of the component colours. The Lovibond tintometer was found satisfactory for the purpose. It is true as Parsons and Wilson (*Ind. Eng. Chem.*, 1922, **14**, 269) have pointed out that Lovibond colour units are not additive and subtractive in the strictest mathematical sense. But it has also been shown by those investigators that up to 50°L (Lovibond), there is practically no deviation from the true colour as measured by them. In the following investigations no glass above 20°L, has been used and the question of any appreciable error does not therefore arise. We have used $\frac{1}{2}''$ cell for kerosene and $1''$ cell for groundnut oil in the colour measurements. Both the original and the treated oils have been satisfactorily matched against a combination of red and yellow glasses. The percentage of colour removed has been calculated as follows:—If a be the sum of the numbers of glasses of any particular shade required to match against the original oil and b the sum of the numbers of glasses of the same shade required to match the treated oil of the same thickness, then the percentage removal of colour is given by $100(a-b)/a$.

Comparison of the Efficiency of different Adsorbents.—The usual practice is to shake 100 c.c. of a coloured oil with a fixed amount (5 g.) of the different adsorbents and to measure the colour of the treated oil with a tintometer. When the Lovibond tintometer is used for the purpose, the comparative efficiencies of the adsorbents used are calculated as follows:—Suppose the colour of the original oil is 30°L, and those of the portions treated with two adsorbents A and B are 15°L and 10°L respectively. The colour removed by

A is therefore (30°−15°)L and that removed by the same amount of B is 20°L. Hence the efficiency of A to that of B is assumed to be as 15:20. Hence, it is assumed that 4 g. of A would effect the same degree of decolourisation as 3 g. of B. A reference to the curves in Figs. 1A and 1B obtained by plotting amounts of adsorbents along X-axis, and percentage removal of colour along Y-axis, will show that this assumption is inaccurate and does not agree with the actual experimental data. It will also be observed that the decolourisation of kerosene with large amounts of the mixed adsorbent, alumina-silica, is greater than with the corresponding amounts of bone charcoal, but the case is different when the amounts of the adsorbents are small. This fact and the different degree of bendings in the curves for different adsorbents clearly show that the assumption of a constant efficiency ratio between two adsorbents is untenable.

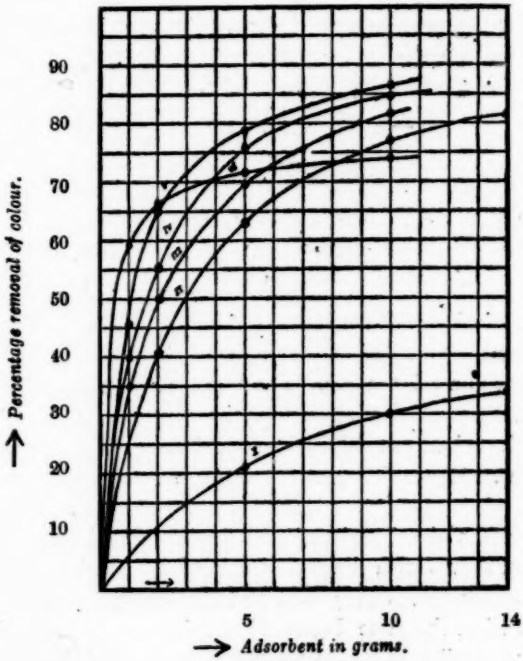


Fig. IA.

Composition of different adsorbents for red colour.

I = Bauxite ; II = Bauxite-silica II; III = Alumina-silica V; IV = Alumina-silica, II; V = Alumina-silica III; VI = Bone charcoal.

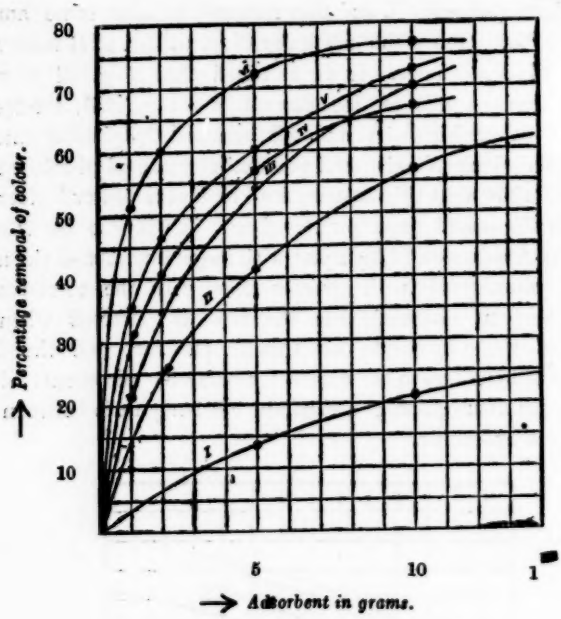


Fig. IB.

Comparison of different adsorbents for yellow colour.

I = Bauxite; II = Bauxite-silica II; III = Alumina-silica V; IV = Alumina-silica I; V = Alumina-silica III; VI = Bone charcoal.

Another method for the comparison of adsorbents is to treat an oil with different amounts of adsorbents until the filtered oils show the same colour in a colorimeter. The practical difficulties in regulating the quantities of adsorbents until the same colour is obtained are great, as the colour can only be measured after filtration following each treatment. Hence this method finds little favour in actual practice.

The best means of comparing the efficiencies is to draw complete decolourisation curves with different amounts of adsorbents. From a reference to such curves (Fig. I, A and B) the quantities of the adsorbents to effect the same degree of decolourisation or the degree of decolourisation effected by the same amounts of adsorbents may easily be found. It will be further observed that the steeper the slope of a curve for smaller quantities of an adsorbent, the better the adsorbent when used as a decolouriser.

The activities of different adsorbents on coloured kerosene (sample no. 1) may be compared from the following tables and the corresponding graphs in Fig. I, A and B.

TABLE IA.

Comparison of different adsorbents (for red colour).

Vol. of kerosene no. 1 = 100 c.c. havingred colour = 2·7°L and yellow colour = 16·5°L.

	Bauxite.		*Bauxite-silica mixture II.*		*Bone charcoal.*	
Adsorbent in g.	Colour observed.	Removal of colour.	Colour observed.	Removal of colour.	Colour observed.	Removal of colour.
1	—	—	—	—	1·1°L	59·26%
2	—	—	1·6°L	40·74%	0·9	66·67
5	2·15°L	20·37%	1·0	62·96	0·8	70·37
10	1·9	29·63	0·62	77·03	0·7	74·07
20	1·65	38·89	0·42	84·44	—	—
30	1·6	40·74	—	—	—	—
	Alumina-silica mixture II.		*Alumina-silica mixture III.*		*Alumina-silica mixture V.*	
1	1·65	38·89	1·5	44·44	1·75	35·19
2	1·2	55·56	0·92	65·93	1·35	50·00
5	0·65	75·93	0·62	77·03	0·82	69·63
10	0·43	84·07	0·35	87·03	0·5	81·48

TABLE IB.

Comparison of different adsorbents (for yellow colour).

(Data observed in simultaneous measurements with Table IA.)

	Bauxite.		*Bauxite-silica mixture II.*		*Bone charcoal.*	
Adsorbent in g.	Colour observed.	Removal of colour.	Colour observed.	Removal of colour.	Colour observed.	Removal of colour.
1	—	—	—	—	8·0°L	51·52%
2	—	—	12·0°L	27·27%	6·6	60·00
5	14·2°L	13·94%	9·8	40·61	4·5	72·73
10	13·0	21·21	7·0	57·58	3·8	76·97
20	11·8	28·48	5·0	69·70	—	—
30	11·3	31·52	—	—	—	—
	Alumina-silica mixture II.		*Alumina-silica mixture III.*		*Alumina-silica mixture V.*	
1	11·3	31·52	10·8	34·55	13·0	21·21
2	9·8	40·61	8·8	46·67	10·8	34·55
5	7·1	56·97	6·6	60·0	77·6	53·94
10	5·5	66·67	4·5	72·73	5·0	69·70

The adsorption curves for pure alumina and silica are not shown above. Decolourisation with these materials is slight and is of the same order as that observed with bauxite. It will be observed from the figures given above that the adsorption of red and yellow colours are not identical. In some cases more red is adsorbed while in others more yellow, exactly as is to be expected from the well known specific nature of adsorbents.

Incidentally the above tables furnish figures for testing the applicability of Freundlich's equation

$$\frac{x}{m} = kc^{\frac{1}{n}} \quad \text{or} \quad \log x/m = \log k + 1/n \log c.$$

where x = amount of colour removed separately for each component colour red or yellow;

m = grams of adsorbent used for 100 c.c. of oil;

c = amount of colour remaining in the solution after adsorption; and k and n are constants dependent upon the solution and the adsorbent used.

The following table gives the values for $\log x/m$ and $\log c$, as calculated from the data of the previous table. The difference between the observed colour and the original colour has been taken as x, c being obviously the observed colour.

TABLE IIA (for red colour).

The values deduced from correponding figures of Table IA (for red colour).

	Bauxite.		*Bauxite-silica mixture II.*		*Bone charcoal.*	
Adsorbent in g.	$\log x/m$.	$\log c$.	$\log x/m$.	$\log c$.	$\log x/m$.	$\log c$.
1	—	—	—	—	0·2041	0·0414
2	—	—	−0·2596	0·2041	−0·0458	−0·0458
5	−0·9586	0·3324	−0·4685	0·0000	−0·4202	−0·0969
10	−1·0969	0·2788	−0·6819	−0·2076	−0·6990	−0·1549
20	−1·2798	0·2175	−0·9431	−0·3768	—	—
30	−1·4353	0·2041	—	—	—	—

TABLE IIA—*continued.*

Adsorbent in g.	*Alumina-silica mixture II.* log x/m.	log c.	*Alumina-silica mixture III.* log x/m.	log c.	*Alumina-silica mixture V.* log x/m.	log c.
1	0·0212	0·2175	0·0792	0·1761	−0·0223	0·3430
2	−0·1249	0·0792	−0·0506	−0·0362	−0·1707	0·1303
5	−0·3872	−0·1871	−0·3809	−0·2076	−0·4248	−0·0862
10	−0·6440	−0·3665	−0·6289	−0·4559	−0·6576	−0·3010

TABLE IIB (for yellow colour).

The values deduced from the corresponding figures of Table IB (for yellow colour).

Adsorbent in g.	*Bauxite.* log x/m.	log c.	*Bauxite-silica mixture II.* log x/m.	log c.	*Bone charcoal.* log x/m.	log c.
1	—	—	—	—	0·9294	0·9031
2	—	—	0·3522	1·0792	0·6946	0·8195
5	−0·3372	1·1523	0·1271	0·9912	0·3802	0·6532
10	−0·4559	1·1139	−0·0223	0·8451	0·1038	0·5798
20	−0·6289	1·0719	−0·2403	0·6990	—	—
30	−0·7612	1·0531	—	—	—	—

	Alumina-silica mixture II.		*Alumina-silica mixture III.*		*Alumina-silica mixture V.*	
1	0·7160	1·0531	0·7559	1·0334	0·5441	1·1139
2	0·5250	0·9912	0·5855	0·9445	0·4548	1·0334
5	0·2742	0·8513	0·2967	0·8195	0·2504	0·8808
10	0·0414	0·7404	0·0792	0·6532	0·0607	0·6990

To test the general applicability of mixed decolourisers in conformity with Freundlich's rule a different sample of kerosene oil was treated with varying amounts of adsorbents. Results are given in the following table.

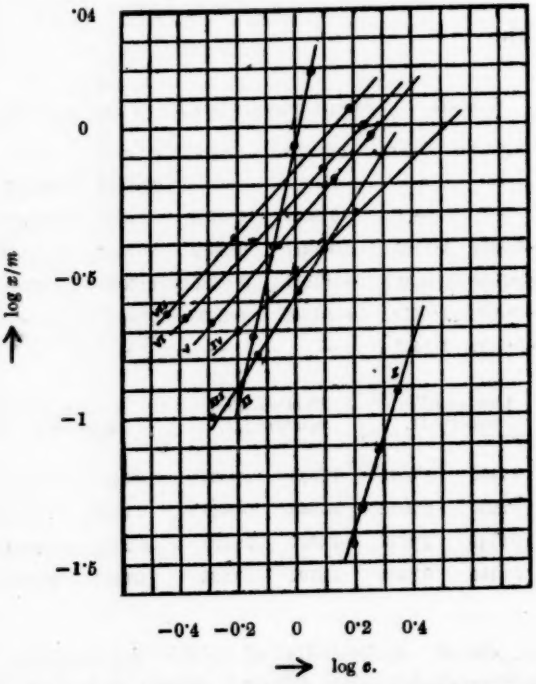
TABLE IIC.

Adsorbent used—Alumina-silica mixture II.
Vol. of kerosene sample no. II=100 c.c.
Original colour—red=1·6°L and yellow=20°L.

	Red colour.			*Yellow colour.*		
Adsorbent in g.	Colour observed.	log x/m.	log c.	Colour observed.	log x/m.	log c.
1	1·2°L	−0·3979	0·0792	15°L	0·6990	1·1761
2	1·0	−0·5229	0·0000	13	0·5441	1·1139
5	0·72	−0·7545	−0·1427	9·8	0·3096	0·9912
10	0·50	−0·9586	−0·3010	7·6	0·0934	0·8808

Fig. II.

Adsorption isotherm for red.



I=Bauxite ; II=Bone charcoal ; III=Alumina-silica II ;
IV=Bauxite-silica II ; V=Alumina-silica V ; VI=Alumina-silica II ;
VII=Alumina-silicia III.

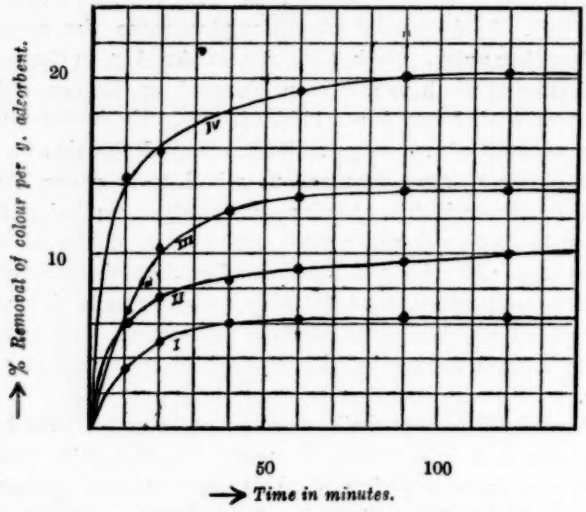
It will be seen from the curves (Fig. II) that only straight lines are obtained by plotting log x/m against log c. The values of $1/n$, that is, the tangents of the angles of inclination of the curves to the log c-axis are found to be greater than unity (because no angle is less than 45°). In the general adsorption phenomena the values of $1/n$ are less than unity. Such high figures for $1/n$ in the case of decolourisation of oils have also been observed by Rogers, Grimm and Lemmon (*Ind. Eng. Chem.*, 1926, **18**, 164). Unlike the general rule, the amount of colouring matters adsorbed in this case, is proportional to c (colour concentration) raised to a power greater than unity. Freundlich's equation is therefore applicable in the adsorption of both red and yellow components of the colour of kerosene only with this modification. The fact that the amount adsorbed is proportional to c raised to a power greater than unity, explains clearly why it is so very difficult to remove the last traces of colour from kerosene by the method of adsorption in actual practice.

Another significance of the log-curves may be noted. The higher the efficiency of a decolouriser the more upward parallel displacement its log-curve experiences. This gives a good picture for comparative decolourising efficiencies of adsorbents.

Velocity of Decoloruisation.—In the previous experiments the oil was shaken with decolourisers until the colouring matter was no more adsorbed. It is however desirable to investigate the time required to attain the equilibrium by different adsorbents. The following tables give the data of experiments with this end in view. The rate of shaking, size of particles, etc., have been kept constant. The influence of temperature in the case of solid-liquid interface being only slight for small variations of temperature, the necessity of a thermostat was dispensed with and the experiments were conducted at room temperature. It will be observed that the equilibrium is mostly attained in 1½ hours. The time of contact in all experiments has been kept at 2 hours in order to ensure complete adsorption in each case. The nature of the curves (Fig. III) is similar to those usually found for adsorption velocity curves (Freundlich, "Colloid and Capillary Chemistry," p. 108), although the equilibrium is attained after a comparatively long time and not in seconds orminutes.

Velocity of adsorption.

Fig. III.



I = Bauxite-silica III (yellow). II = Bauxite-silica III (red).
III = Bauxite-silica II (yellow). IV = Bauxite-silica II (red).

TABLE IIIA.

Velocity of adsorption.

Adsorbent—Bauxite-silica mixture II (21·88% SiO_2): 2 g. for 100 c.c. kerosene no. I.

Colour—red = 2·7°L and yellow = 16·5°L.

	Red colour.		*Yellow colour.*	
Time of shaking.	Colour observed.	Colour removed per g. of adsorbent.	Colour observed.	Colour removed per g. of adsorbent.
10 mins.	1·9°L	14·82%	14·2°L	6·97%
20 ,,	1·87	15·37	13·0	10·61
40 ,,	1·72	18·15	12·5	12·12
60 ,,	1·65	19·44	12·0	13·64
90 ,,	1·60	20·37	,,	,,
2 hrs.	,,	,,	,,	,,
4 ,,	,,	,,	,,	,,

TABLE IIIB.

Adsorbent—Bauxite-silica mixture III (30·8% SiO_2) : 4 g. per 100 c.c. kerosene no. I.

	Red colour.		*Yellow colour.*	
Time of shaking.	Colour observed.	Colour removed per g. of adsorbent.	Colour observed.	Colour removed per g. of adsorbent.
5 mins.	2·15°L	5·09%	14·8°L	2·58%
10 ,,	2·00	6·48	14·2	3·48
20 ,,	1·90	7·41	13·0	5·30
40 ,,	1·8	8·33	12·5	6·06
1 hr.	1·72	9·07	,,	,,
1½ hrs.	,,	,,	12·0	6·82
2 ,,	1·6	10·19	,,	,,
4 ,,	,,	,,	,,	,,

Relation between Composition and Activity of Mixed Adsorbents.—It will be observed from Tables IIIA, and IIIB, that the relative proportions of the constituents in silicalised bauxite affect the degree of decolourisation to a great extent. Similar observations have also been made by Chowdhury and Bagchi and by Chowdhury and Pal (*locc. cit.*). It is therefore necessary to find out the most suitable composition of mixed decolourisers and to test their activities both for mineral and vegetable oils. The mixed decolourisers investigated are :—

1. Bauxite—silica;
2. Alumina—silica;
3. Carbon—alumina.

Mixed adsorbents have been prepared, by the precipitation of one adsorbent upon another suspended in finely divided form.

Preparation of the Mixed Adsorbents.

1. *Silicalised Bauxite.*

The bauxite used gave the following figures:—Al_2O_3, 59·2; Fe_2O_3, 3·8; SiO_2, 19·2, TiO_2, 3·7; moisture, 11·8 per cent. ; Ca, traces; Mg, traces.

For the preparation of silicalised bauxite of different compositions, the bauxite was finely powdered, and suspended in the usual

manner in a 4·94 per cent. solution of sodium silicate, the silica precipitated with a 10 per cent. solution of hydrochloric acid under constant stirring (mechanical), filtered and washed thoroughly. The different adsorbents thus obtained were pressed, dried in the air and subsequently at 60°, in a steam-oven. This mode of drying has been found to be particularly suitable for the preparation of the mixed adsorbents, as well as of the pure gels. The absorbents were used for decolourisation in the form of fine granules (80-160 mesh per sq. inch) after the final activation at suitable temperatures in a furnace, in the presence of a current of dry air so as to reduce their water-content to a suitable percentage.

The percentages of silica (deposited) as found on analysis of the mixtures and their moisture contents are shown in the following table which contains figures to show the relationship between composition and activity of the mixed bauxite-silica adsorbents.

TABLE IV.

Decolourisation with silicalised bauxite of different compositions.
Adsorbent used—5 g. for 100 c. c. kerosene no. I, of red colour= 2·7°L, and yellow colour=16·5°L. Time of shaking=2 hrs.

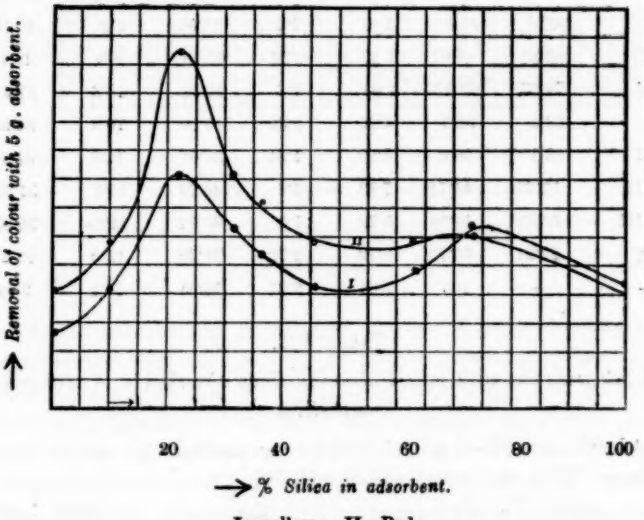
	Percentage composition of mixtures.			*Red colour.*		*Yellow colour.*	
No. of mixture.	Bauxite.	Silica.	Moisture.	Colour obs.	Colour removed.	Colour obs.	Colour removed.
I	100%	—	9·73%	2·15°L	20·37%	14·2°L	13·94%
I	89·91	10·09%	9·76	1·9	29·63	13·0	21·21
II	78·12	21·88	9·23	1·0	62·96	9·8	40·61
III	69·18	30·82	8·8	1·6	40·74	11·3	31·52
IV	64·1	35·9	9·1	1·72	36·29	12·0	27·27
V	54·36	45·64	9·26	1·9	29·63	13·0	21·21
VI	37·32	62·68	8·77	1·9	29·63	12·5	24·24
VII	26·31	73·69	7·94	1·87	30·74	11·3	31·52
—	—	100	6·0	2·15	20·37	13·0	21·21

The increase in the figures for decolourisation is remarkable, the maximum results being obtained with 21·88 per cent. silica. A mere mechanical mixture of the two decolourisers has no increased efficiency, as individually both of them have but poor decolourising

power. That the observed increase in efficiency of the mixed adsorbents is not due to a slight variation of the water contents from mixture to mixture will find confirmation from the data given in a subsequent section for the effect of moisture contents of the decolourisers. A clear picture of the variation of efficiency of the mixed adsorbents will be obtained with reference to the curves of Fig. IV. A reference to Fig. I, A and B, will show what a great increase in activity, bauxite has undergone by the addition of 21·88 per cent. of silica.

Decolourisation of kerosene with silicalised bauxite of different composition.

Fig. IV.



I=yellow; II=Red.

2. *Alumina-silica Mixtures.*

For the preparation of alumina-silica mixtures of different compositions, undried silica gel was suspended in a 10 per cent. solution of aluminium sulphate and aluminium hydroxide was precipitated with ammonia under constant stirring (mechanical). Washing the gels free from acid, drying, activation etc., were similar to those described above for mixed bauxite-silica adsorbents. The percentage composition as found on analysis and water-content of different

gel-mixtures are shown in the following tables, giving data for the variation of efficiency of the mixed adsorbents with composition.

TABLE VA.

Decolourisation with mixed alumina-silica adsorbents of different compositions.

Adsorbent used—2 g. per 100 c.c. kerosene no. I, of red colour =2·7°L, and yellow colour=16·5°L.

	Composition of mixtures.			*Red colour.*		*Yellow colour.*	
No. of mixture.	Silica.	Alumina.	Moisture.	Colour obs.	Colour removal.	Colour obs.	Colour removal.
—	100%	—	6·0%	2·5°L	7·41%	15·0°L	9·09%
I	94·04	5·96%	7·23	1·6	40·74	10·8	34·55
II	90·01	9·99	5·81	1·2	55·56	9·8	40·61
III	83·33	16·67	7·46	0·92	65·93	8·8	46·70
IV	74·87	25·13	6·33	1·2	55·56	10·3	37·58
V	63·3	36·7	5·25	1·35	50·00	10·8	34·55
VI	63·1	36·9	4·89	1·35	50·00	10·8	34·55
VII	53·25	46·74	7·83	1·6	40·74	10·8	34·55
VIII	53·21	46·79	5·72	1·6	40·74	11·05	33·03
IX	23·21	76·79	6·12	1·72	36·29	12·0	27·27
—	—	100	7·64	2·27	15·93	15·0	9·09

TABLE VB.

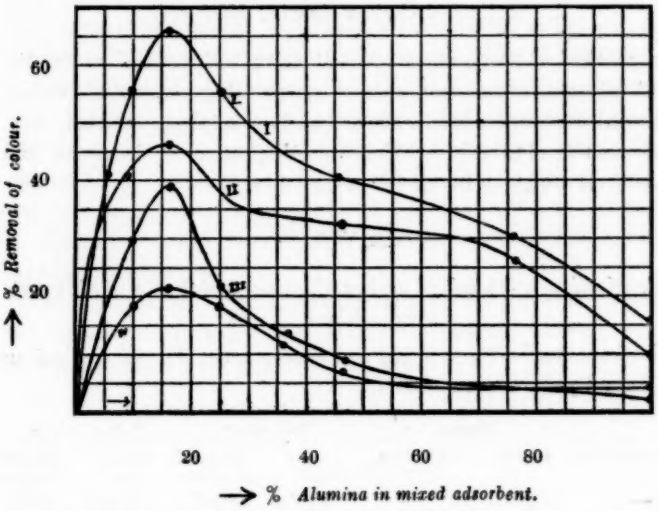
Decolourisation with mixed alumina-silica absorbents of different composition.

Adsorbent used—5 g. per 100 c.c. groundnut oil no. I, of red colour=1·72°L and yellow colour=12·5°L.

	Composition of mixtures.			*Red colour.*		*Yellow colour.*	
No. of mixture.	Silica.	Alumina.	Moisture.	Colour obs.	Colour removal.	Colour obs.	Colour removal.
—	100%	—	6·0%	1·72°L	—	12·5°L	—
II	90·01	9·99%	5·81	1·40	18·6%	8·8	29·6%
III	83·33	16·67	7·46	1·35	21·51	7·6	39·2
IV	74·87	25·13	6·33	1·4	18·6	9·8	21·6
VI	63·1	36·9	4·89	1·5	12·79	10·8	13·6
VIII	53·21	46·79	5·72	1·6	6·98	11·3	9·6
IX	23·21	76·79	6·12	1·65	4·07	12·0	4·0
—	—	100	7·64	1·65	4·07	12·5	—

Decolourisation with mixed alumina-silica of different composition.

Fig. V.



I = Removal of red in kerosene no. I, using 2 g. adsorbent per 100 c.c.
II = ,, yellow ,, ,, ,, ,,
III = ,, ,, groundnut oil 5 g. ,, ,,
IV = ,, red ,, ,, ,, ,,

While either silica or alumina is but a poor decolouriser for kerosene oil and particularly so for groundnut oil, quite a striking increase in the activity has been obtained from intimate mixtures of the two. The data of the above tables, plotted in Fig. V, manifest this fact in a clear manner. The maximum efficiency is reached both for kerosene and groundnut oil in the mixture III containing 83·3 per cent. silica and 16·67 per cent. alumina. It is interesting to note that the order of efficiency of the different mixed adsorbents is strictly maintained in the decolourisation of both kerosene and groundnut oil. It will be observed from the curves that besides the optimum mixture other mixtures of composition varying over a large range have remarkable increase in activity over that of the pure silica or alumina. A reference to the curves in Fig. I, A and B, for different alumina-silica mixtures and bone charcoal, will show that the mixed adsorbent alumina-silica III (optimum mixture) is of the same order of efficiency as bone charcoal and the other mixtures also are not much inferior to it. These mixed adsorbents

have on the other hand many advantages over bone charcoal such as those usually claimed for the most inorganic adsorbents.

3. *Activated Carbon-alumina Mixtures.*

The method of preparation and activation is the same as in the case of alumina-silica mixtures, except that activated carbon (Kahlbaum) was suspended in the aluminium sulphate solution.

The results obtained for the decolourisation of kerosene and groundnut oil are given in the following table.

TABLE VIA.

Decolourisation with mixed carbon-alumina adsorbents of different compositions.

Adsorbent used—2 g. per 100 c.c. kerosene no. II, of red colour =1·6°L and yellow colour=20°L.

	Composition.		*Red colour.*		*Yellow colour.*	
No. of mixtures.	Carbon.	Alumina.	Colour obs.	Removal of colour.	Colour obs.	Removal of colour.
—	100%	—	0·70°L	56·25%	10·3°L	48·5%
I	92·7	7·3%	0·62	61·25	10·3	48·5
II	86·7	13·3	0·62	61·25	10·3	48·5
III	67·2	32·8	0·82	48·75	11·3	43·5
IV	38·4	61·6	0·92	42·50	13·0	35·0
V	25·2	74·8	1·00	37·5	13·5	32·5
—	—	100	1·4	12·5	18·0	10·0

TABLE VIB.

Decolourisation with mixed carbon-alumina adsorbents of different compositions.

Adsorbent used—5 g. per 100 c.c. groundnut oil no. II of red colour =1·6°L and yellow colour=6·6°L.

	Composition.		*Red colour.*		*Yellow colour.*	
No. of mixtures.	Carbon.	Alumina.	Colour obs.	Removal of colour.	Colour obs.	Removal of colour.
—	100%	—	0·8%	50·0%	2·2°L	66·67%
I	92·7	7·3%	0·8	50·0	2·2	66·67
II	86·7	13·3	0·8	50·0	2·2	66·67
III	67·2	32·8	0·85	46·88	2·3	66·67
IV	38·2	61·6	1·1	31·25	2·8	57·58
V	25·2	74·8	1·35	15·63	5·0	24·24
—	—	100	1·6	—	6·0	9·09

In the case of activated carbon-alumina mixtures the increase over the efficiency of carbon is rather slight, but it will be observed that quite a large percentage (about 30%) of costly activated carbon may easily be replaced by alumina without loss of efficiency. The activity is however always more than that calculated from the composition of a mechanical mixture of the two adsorbents on the supposition that the activity of each adsorbent is independent of the other. This increase is more remarkable when alumina predominates in the mixtures. The coating of alumina on the surface of carbon has the further advantage as observed by Berl (D.R.P. 375658) that it decreases the inflammability of activated carbon—generally of pyrophorous nature.

The effect of ferric hydroxide on alumina was also investigated. No increase in efficiency was however observed. Ferric hydroxide in itself is also a poor decolourising agent.

The Effect of Temperature of Roasting and Water Contents of the Decolourisers.

It is desirable to investigate how far the activities of the above mixed adsorbents depend on the temperature of roasting and the consequent variation of water content. The literature in connection with the temperature to which an adsorbent should be heated for the purpose of proper activation is full of contradictory reports. Thus Parsons ("Fuller's Earth," 1913) does not recommend any heating at all for Fuller's earth, while Deckert (*Seifensied. Ztg.*, 1925, **52**, 754) has obtained best results by heating Fuller's earth to 500°—600°. Munro and Johnson (*Ind. Eng. Chem.*, 1925, **17**, 88) recommend a temperature of 400° for alumina gel; Perry (*J. Phys. Chem.* 1925, **29**, 1462) a temperature of 200°; while Dunstan and others (*J. Soc. Chem. Ind.*, 1924, **43**, 179T,) a temperature of 600° for bauxite.

Several investigators have also noted the rôle of water content adsorbents. Thus Patrick and McGavack (*loc. cit.*) have observed that a small amount of moisture is always associated with silica gel for efficient adsorption of sulphur dioxide and water vapour. Roy (*J. Phys. Chem.*, 1925, **29**, 75) has found that silica gel with 5% water displays the greatest activity for N_2O_4. Munro and Johnson (*loc. cit.*) find the presence of 4·5—7% water in alumina necessary for best adsorption of gases and vapours. Similar results

showing the influence of water on adsorption in solid-liquid interface have also been observed in the case of floridin (Gurwitsch, "Scientific Principles of Petroleum Technology," p. 406).

The following table contains data of experiments conducted with a view to ascertain the rôle of temperature of roasting and water content in the adsorbents.

TABLE VIIA.

Variation of efficiency of bauxite with temperature of roasting and water content.

Adsorbent used—5 g. per 100 c.c. kerosene no. I, of red colour =2·7° and yellow colour=16·5°L.

		Red colour.		*Yellow colour.*	
Temperature of roasting.	Moisture remaining.	Colour obs.	Colour removed.	Colour obs.	Colour removed.
—	11·8%	2·45°L	9·37%	15·0°L	9·09%
275°-300°	9·73	2·15	20·37	14·2	13·94
350°-400°	8·12	2·15	20·37	14·2	13·94
400°-500°	6·33	2·15	20·37	13·5	18·18
Strong ignition	—	2·15	20·37	13·5	18·18

TABLE VIIB.

Variation of efficiency of bauxite-silica II (silica, 21·88%) with temperature of roasting and water content.

Adsorbent used—5 g. per 100 c.c. kerosene no. I.

		Red colour.		*Yellow colour.*	
Temperature of roasting.	Moisture remaining.	Colour obs.	Colour removed.	Colour obs.	Colour removed.
60°	20·39%	1·6°L	40·74%	12·5°L	24·24%
150°	12·23	1·1	59·26	10·8	34·54
250°	9·23	1·0	62·96	9·8	40·61
275°-300°	7·58	1·0	62·96	9·8	40·61
400°-500°	5·95	0·92	65·93	9·8	40·61
Strong ignition	—	1·1	59·26	10·8	34·54

TABLE VIIC.

Variation of efficiency of alumina-silica III (silica, 83·3%) with temperature of roasting and water content.

Adsorbent used—2 g. per 100 c.c. kerosene no. I, of red colour =2·7° and yellow colour=16·5°L.

		Red colour.		*Yellow colour.*	
Temperature of roasting.	Water content.	Colour obs.	Colour removed.	Colour obs.	Colour removed.
60°	22·55%	1·6°L	40·74%	12·0°L	27·27%
150°	7·46	0·92	65·93	8·8	46·67
175°	4·27	0·92	65·93	7·6	53·94
250°	2·29	0·95	64·81	9·3	43·64
300°	1·87	1·1	59·26	9·3	43·64
Strong ignition	—	1·35	50·00	9·8	40·61

It will be seen from the above figures that completely dried adsorbents have less activity than partially dried ones. Thus the power of decolourisation attains a maximum with 6·33% of water in the case of bauxite, 5·95% in the optimum bauxite-silica mixture and 4·27% in the optimum alumina-silica mixture. The percentage of moisture content and temperature of roasting are interdependent. At any particular temperature it is very difficult even after prolonged drying to drive off more than a certain percentage of water and it seems as if an equilibrium is reached in the moisture content of each adsorbent.

Regeneration of Adsorbents.

The mixed adsorbents must be capable of repeated regeneration for industrial use. In this respect the inorganic decolourisers have an advantage over activated carbon and animal charcoal which in-spite of their high decolourising value, are costly to revivify. We have regenerated the mixed adsorbents after ten successive treatments and found that the regenerated adsorbents have suffered only very slightly in their activity. The usual methods of treatment with steam and air has been found quite satisfactory. A preliminary treatment with water which is adsorbed in preference and drives out the major portion of the adsorbed material from the decolourisers has

also been found to give satisfactory results (*cf.* Gurwitsch, *loc. cit.*, p. 415). The mass is subsequently roasted in a current of air, or if the temperature is to be kept to the minimum possible level in a mixture of steam and air. It will be observed that after the first regeneration the activity of the mixed adsorbent slightly deteriorates, but further repeated regeneration has little injurious effect, if any. The decolouriser has been revivified 10 times with little loss of efficiency. The experimental data are given in the following table:—

TABLE VIII.

Regeneration of the mixed decolouriser alumina-silica II.

Adsorbent—2 g. per 100 c.c. kerosene no. II, of red colour=1·6° and yellow colour=20°L.

	Red colour.		*Yellow colour.*	
No. of treatments.	Colour obs.	Colour removed.	Colour obs.	Colour removed.
1st	1·0°L	37·5%	13·0°L	35·0%
2nd	1·1	31·25	13·5	32·5
3rd	,,	,,	,,	,,
4th	,,	,,	,,	,,
5th	,,	,,	,,	,,
6th	,,	,,	,,	,,
7th	,,	,,	,,	,,
8th	,,	,,	,,	,,
9th	,,	,,	,,	,,
10th	,,	,,	14·2	29·0

Discussion.

It is generally agreed that adsorption is a physical phenomenon. As regards the mechanism of adsorption there are two principal theories. Zsigmondy, Patrick and other investigators maintain that adsorption is maily due to capillary forces. In cases where the pores are of the nature of a cone, adsorption takes place at the narrow ends which are filled with the adsorbed substance, while the wider portions remained unoccupied. It may be imagined that in the mixed adsorbents the wider portions of the pores of one adsorbent are filled up

with another adsorbent deposited on it, thus forming a large number of narrow capillaries. This would also explain the fact that mechanical mixtures of the adsorbent have no increased efficiency. According to this theory, it would however be difficult to account for the fact that little or no increase of activity is noticed when iron hydroxide is precipitated on aluminium hydroxide. The chemical nature of the constituents evidently plays an important part. It will be noticed that best results are obtained when silica gel which is acidic in nature is deposited on alumina or bauxite of basic character.

The adsorption phenomenon have been explained in recent years by ordinary laws of molecular attraction (Eucken, *Verh. deut. physikal Ges.*, **16**, 349, *Z. Elektrochem.*, 1922, **28**, 6 ; Polanyi, *Verh. deut. physikal Ges.*, 1916, **18**, 55 ; Lorenz and Lande, *Z. anorg. Chem.*, 1922, **125**, 4). It is believed that this molecular attraction depends on the dipolar nature of most molecules. Dipolarity may also be induced in the molecules, of most substances, when they come under the influence of outside electric forces or in the proximity of other molecules. The intensity of attraction depends not only on the moments of the dipolar molecules coming within each other's influence, but also on the inclination which their axes form with one another. The adsorption potential depends on the distance of the dipolar molecules from the solid adsorbent surface, and on the angles which their axes build with the perpendicular on the adsorbent surface. These angles will naturally depend on the temperature, as the position of the axes will be disturbed by heat. In order to explain the comparatively small influence of temperature on adsorption, it is assumed that the forces of disturbance that would be caused by little differences in temperature, are very small in comparison with the forces of attraction.

Hence, the function of the adsorbent is mainly to expose a large surface and thus to provide a large number of molecules to influence the molecules of the material to be adsorbed. The electric properties of the adsorbent, such as its conductivity or dielectric constant would naturally have some influence on adsorption. But how far these electrical properties of different adsorbents affect the adsorption capacity is unfortunately extremely difficult to determine experimentally. It is not improbable that the presence of water in the adsorbents materially affect these electrical properties. It can easily be understood that the presence of large amounts of water will prevent the molecules of the adsorptive from coming in close

proximity with the molecules of the adsorbent, and hence the necessity for drying; but the complete absence of water will affect the above-mentioned electrical properties of the adsorbents and may injuriously affect the adsorption capacity. This may be a likely explanation for the presence of small amounts of water in the adsorbents, —a fact for which no satisfactory explanation is available.

In the mixed adsorbents it is reasonable to assume that narrow capillary canals are formed, the two walls of which are oppositely charged and therefore create an electric field within the pores, similar to electric condensers. Under the influence of this field the molecules of the adsorptive become dipolar and are therefore systematically arranged in the canals, thus increasing the amount of adsorption. When the walls are of the same charge the molecules attaching themselves to the surface will be similarly charged, and will repel one another, when in close proximity. They will therefore diminish the forces of adsorption or prevent other molecules from coming in to fill up the intervening space. The case is however different when the walls are of opposite charges. As the adsorbed molecules are now oppositely charged no repulsion takes place and other dipolar molecules will be attracted to fill up the intervening space, if any. Thus in Fig. VI, where both the walls are of the same charge, the

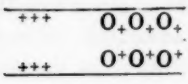


Fig. VI.

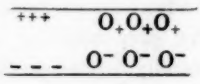


Fig. VII.

dipolar molecules attaching to the surfaces will each be positively charged. These molecules will repel each other or prevent the filling up of intervening space by other molecules. In Fig. VII, where the walls are oppositely charged the molecules attaching themselves to the walls will also be oppositely charged. Other dipolar molecules will therefore be attracted to fill up the intervening space and the axes of all the adsorbed molecules will be systematically arranged and the adsorption capacity will increase.

In conclusion, our best thanks are due to the Director of Geological Survey, Calcutta, for kindly supplying us with bauxite from the Central Provinces for the purpose of these experiments.

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Condensations of Levulinic Acid with Aldehydes.

By Rajendra Nath Sen and Biresh Chandra Roy.

In the present investigation condensations of levulinic acid with various aldehydes have been systematically studied; and as a result, three distinct types (α, β and δ) of condensation products have been obtained, the last two of these giving rise to interesting ring-compounds on further condensation.

Levulinic acid yielded β-condensation products with benzaldehyde (Erdman, *Ber.*, 1885, **18**, 3441) and with furfuraldehyde (Erdman and Kehrer, *Ber.*, 1893, **26**, 345) in the presence of fused sodium acetate. Erdman's β-benzylidinelevulinic acid (m.p. 125°) has now been obtained much more easily and in much greater yield using dry hydrochloric acid gas as the condensing agent. Similar β-condensations with other aldehydes in presence of the acid at the ordinary temperature have also been systematically studied.

By condensing levulinic acid with benzaldehyde (Erlenmeyer, *Ber.*, 1890, **23**, 74), furfuraldehyde (Ludwig and Kehrer, *Ber.*, 1891, **24**, 276) and *iso*butylaldehyde (Meigash, *Monatsh.*, 1905, **26**, 2675) in the presence of dilute caustic soda solution δ-condensation products were previously obtained. Similar δ-condensations with different aldehydes have now further been studied.

Borsche (*Ber.*, 1915, **48**, 842) observed that when the sodium salt of the acid is heated with benzaldehyde in the presence of acetic anhydride, the reaction takes place at the α-position. Similar α-condensation products have been obtained by the condensation of levulinic acid with different aldehydes.

$\alpha\beta$-, $\alpha\delta$- and $\beta\delta$-condensations have also been successfully effected in many cases with the formation of dibenzylidene compounds by carrying out the reaction successively with different condensing agents.

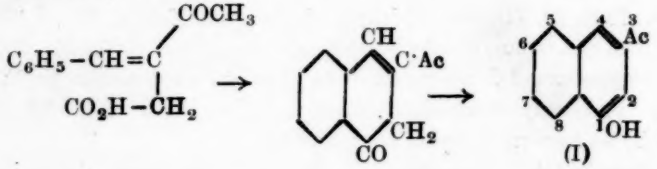
Studies of these dibenzylidene compounds have proved very useful in obtaining further evidence of the condensations taking place in different positions with different condensing agents. Thus the identical $\beta\delta$-dibenzylidene compound, $Ph{\cdot}CH{=}CH{\cdot}CO{\cdot}C(:CHPh){\cdot}CH_2{\cdot}CO_2H$ is obtained by condensing a second molecule of benzaldehyde either

with β-benzylidenelevulinic acid in presence of caustic soda or with δ-benzylidenelevulinic acid in presence of dry hydrochloric acid gas. But the dibenzylidene derivative, $Ph{\cdot}CH{=}CH{\cdot}CO{\cdot}C(:CH{\cdot}C_6H_4NO_2).CH_2CO_2H$ obtained from β-nitrobenzylidenelevulinic acid and benzaldehyde in the presence of caustic soda is not identical but isomeric with the compound $NO_2{\cdot}C_6H_4{\cdot}CH{=}CH{\cdot}CO{\cdot}C(:CHPh){\cdot}CH_2{\cdot}CO_2H$ obtained from δ-nitrobenzylidenelevulinic acid and benzaldehyde in the presence of dry hydrochloric acid gas.

The αβδ-tribenzylidene compound has also been prepared by condensing the sodium salt of βδ-dibenzylidenelevulinic acid with benzaldehyde in presence of acetic anhydride.

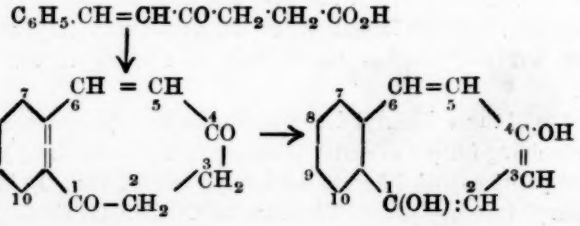
A study of these condensations shows that the hydrogen atoms attached to the β-carbon atom are most reactive while those attached to the α-carbon atom react least readily.

The β- and δ-condensation products (Table I) have also afforded excellent opportunities of studying the possibilities of ring-formation by the action of suitable dehydrating agents; thus, using acetic anhydride, several interesting naphthalene derivatives (Table II) have been obtained from the β-condensation products (*cf.* Erdman, *Ber.*, 1889, **21**, 635, who obtained 3-aceto-1-naphthol from β-benzylidenelevulinic acid).



(I)

The δ-condensation products under similar circumstances have yielded a new type of cyclic compounds (Table III) which may be looked upon as being formed by the coalescence of an eight-membered ring with a benzene nucleus, thus:



(II) (III)

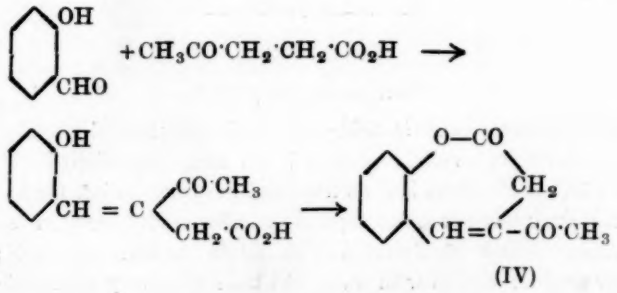
This compound is insoluble in sodium bicarbonate solution (cold or hot) indicating the absence of free carboxyl group; it gives a monophenylhydrazone proving the presence of carbonyl group; its olefinic character is shown by the ready decolorisation of bromine and alkaline permanganate solutions. These facts support the formula (II) for the substance. It is, however, moderately soluble in caustic soda solution in the cold which is presumably due to its tautomerisation to the enolic form (III) as is supported by the formation of a dibenzoyl derivative. This compound also gives a dinitro-derivative. Further studies of this new type of ring-compounds are in progress.

It is interesting to note that when there is an acidic group (NO_2 or OH) in the *m*-position to the aldehyde group, ring formation takes place much more readily; thus δ-*m*-nitrobenzylidene levulinic acid gives the *cyclo*octene derivative at about 100° whereas the corresponding unsubstituted benzylidene compound requires heating up to 120-30°.

This is further corroborated by the action of *m*-hydroxy- and *m*-nitro-benzaldehydes on levulinic acid in presence of dry hydrochloric acid gas when β-condensation takes place followed by ring closure, naphthalene derivatives being obtained at once.

It is remarkable, however, that similar ready ring-formation is also noticed in condensations with piperonal, vanillin and furfuraldehyde, a coumarone derivative being formed in the last case.

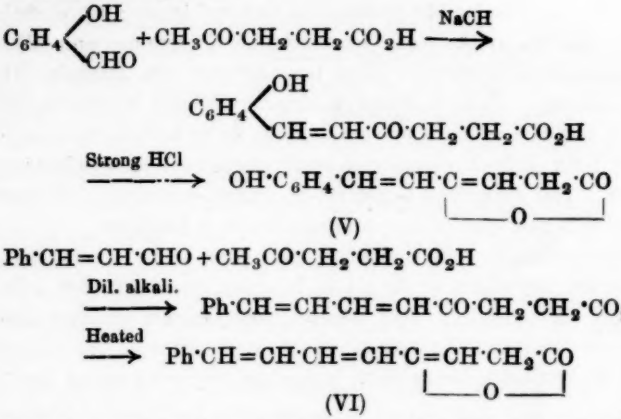
o-Hydroxyaldehydes invariably give seven-membered lactones (Table IV) when condensed with levulinic acid in presence of dry hydrochloric acid gas (β-condensation).



(IV)

The product is insoluble in cold sodium bicarbonate solution and gives a monophenylhydrazone and a dibromo-derivative. On the other hand, five-membered lactones ($\triangle^2$-angelic lactone derivatives)

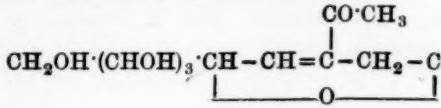
are obtained from the δ-condensation products from salicyl- and cinnamic aldehydes.



Both the compounds are insoluble in cold sodium bicarbonate solution and do not react with phenylhydrazone: the former gives the usual ferric chloride reaction.

It is interesting to note that these lactones are all coloured compounds, the seven-membered lactones possessing deeper colour and also exhibiting marked dyeing properties.

Glucose gives a six-membered lactone when condensed with levulinic acid, through β-condensation:



EXPERIMENTAL.

Open-chain Compounds.

β-Benzylidenelevulinic Acid.—Dry hydrochloric acid gas is passed into a mixture of levulinic acid (5·7 g.) and benzaldehyde (5·3 g.) cooled in ice, for about half an hour and the whole is left for a week when a pitch like substance separates. This is dissolved in caustic soda solution and precipitated with dilute hydrochloric acid; the yellow product washed with water and then with very dilute alcohol. It is finally crystallised from hot dilute alcohol in yellow needles, m.p. 125°, and is found to be identical with Erdman's compound (*loc. cit.*) (yield 70%). (Found: C, 70·62; H, 5·9. $C_{12}H_{12}O_3$ requires C, 70·59; H, 5·89 per cent.).

βδ-Dibenzylidenelevulinic Acid. — β-Benzylidenelevulinic acid (7 g.) and benzaldehyde (6 g.) in 25 c.c. of alcohol and 10 c.c. caustic soda (15 %) are heated on the water-bath for about 2 hours and then acidified with dilute hydrochloric acid in the cold. The precipitate is washed with hot water, then with dilute alcohol and ether and finally crystallised from acetone; it is a yellow micro-crystalline powder, m.p. 146°. It is soluble in alcohol, acetone and chloroform but insoluble in water, ether, benzene, carbon disulphide and carbon tetrachloride (yield, 30%). (Found: C, 77·51; H, 5·19. $C_{19}H_{16}O_3$ requires C, 78·08; H, 5·48 per cent.).

αβ-Dibenzylidenelevulinic Acid.—A mixture of dry sodium salt of β-benzylidenelevulinic acid (1·5 g.) and benzaldehyde (0·8 g.) is heated with acetic anhydride (10 c.c.) on the water-bath for about 20 hours and poured into water; on adding a little alcohol a yellow solid separates out. This is digested with sodium bicarbonate solution, the filtrate acidified with dilute hydrochloric acid and the precipitate crystallised from hot absolute alcohol, when golden-yellow needles are obtained melting at 240°, soluble in acetone and chloroform; they are sparingly soluble in cold alcohol and insoluble in carbon tetrachloride, carbon disulphide, ether, benzene and water (yield, 25%). (Found: C, 77·32; H, 5·30. $C_{19}H_{16}O_3$ requires C, 78·08; H, 5·48 per cent.).

δβ-Dibenzylidenelevulinic Acid.—Dry hydrochloric acid gas is passed into a mixture of an alcoholic solution of Erlenmeyer's δ-benzylidenelevulinic acid (1·5 g.) and of benzaldehyde (1 g.) cooled in ice, and the whole is left for 10 days. The entire mass is then poured into water, the precipitate collected, washed with water, dilute alcohol and ether and finally crystallised from acetone. It is a yellow micro-crystalline powder, m.p. 146°, which is found to be identical with βδ-dibenzylidenelevulinic acid described before. (yield, 40%). (Found: C, 77·67; H, 5·42. $C_{19}H_{16}O_3$ requires C, 78·08; H, 5·48 per cent.).

αδ-Dibenzylidenelevulinic acid has also been prepared by heating a mixture of dry sodium salt of δ-benzylidenelevulinic acid (1·5 g.) and benzaldehyde (1 g.) with acetic anhydride on the water-bath for about 20 hours, the substance being isolated and purified in the same way as the αβ-dibenzylidene acid. It forms light yellow needles m.p. 177°, from hot alcohol (yield, 25—30%). (Found: C, 77·3; H, 5·72. $C_{19}H_{16}O_3$ requires C, 78·08; H, 5·48 per cent.).

αβδ-Tribenzylidenelevulinic Acid.—A mixture of dry sodium salt of *βδ*-dibenzylidenelevulinic acid (3 g.) and benzaldehyde (1 g.) is heated with acetic anhydride (10-12 c.c.) on the water-bath for about 24 hours and poured into dilute alcohol when a yellow solid separates. This is washed with water, dilute alcohol and finally crystallised from acetone. The yellow micro-crystalline powder, melting above 240°, is soluble in alcohol and acetone, sparingly soluble in chloroform and insoluble in water, ether, benzene, carbon disulphide etc. (yield, 20%). (Found: C, 79·96; H, 5·62. $C_{26}H_{20}O_3$ requires C, 80·23; H, 5·83 per cent.).

Other open-chain compounds obtained by condensing levulinic acid with different aldehydes, together with their derivatives are listed in Table I.

Naphthalene Derivatives.

3-Aceto-7-nitro-1-naphthol. — *β-p*-Nitrobenzylidenelevulinic acid (1 g.) is heated with acetic anhydride (10 c.c.) for 3-4 hours at 130-140°. The whole mass is poured into a dilute solution of sodium bicarbonate, cooled with ice and left overnight. The red mass which separates is washed repeatedly with hot water and dilute alcohol and is crystallised from acetone in red micro-crystals, m.p. 189°, which are soluble in acetone, sodium bicarbonate or caustic soda, slightly soluble in alcohol and chloroform but insoluble in water, ether, benzene, etc., and give colouration with ferric chloride (yield, 40%). (Found: N, 6·51. $C_{12}H_9O_4N$ requires N, 6·67 per cent.).

Similar naphthalene derivatives and a coumarone are described in Table II.

New Cyclic Compounds.

Benzo-1:4-diketo-$\triangle^{5:6}$*-cyclo-octene* (II) *or Benzo-1:4-dihydroxy-cyclo-octatetrene* (III) *from Erlenmeyer's δ-Benzylidenelevulinic Acid.*—δ-Benzylidenelevulinic acid (2 g.) is heated with acetic anhydride (10-12 c.c.) at 140-150° for about 4 hours. The entire mass is poured into a very dilute solution of sodium bicarbonate, cooled with ice and left overnight; a red mass that separates is washed repeatedly with hot water and recrystallised from acetone. The red micro-crystals melt at 196°; they are soluble in acetone and chloroform, slightly soluble in alcohol, insoluble in benzene, ether, unaffected by sodium bicarbonate solution cold or hot but dissolve in cold

caustic alkalis. (yield, 40%). (Found: C, 76·95; H, 4·98. $C_{12}H_{12}O_2$ requires C, 77·42; H, 5·38 per cent.).

Hydrazone.—An acetic acid solution of the above substance is heated with phenylhydrazone on the water-bath for half an hour. The solution is then cooled and poured into ice; the yellow solid that separates is washed with chloroform and ether and recrystallised from hot alcohol. At 100° the monohydrazone is always formed even if the time of heating is extended. (Found: N, 9·96. $C_{18}H_{16}N_2O$ requires N, 10·15 per cent.).

Nitro-derivative.—A dinitro-derivative is obtained when glacial acetic acid solution of the substance is treated with concentrated nitric acid at—8 to—10°. Yellow micro-crystals are obtained by recrystallising from hot alcohol (constitution under investigation). (Found: N, 10·11. $C_{12}H_8O_6N_2$ requires N, 10·15 per cent.).

The *dibenzoyl*-derivative is prepared by Schotten-Baumann process and crystallised from alcohol as light yellow powder melting at 160°, soluble in alcohol and acetone but insoluble in ether, chloroform, etc. (Found: C, 79·97; H, 3·99. $C_{26}H_{18}O_4$ requires C, 79·18; H, 4·57 per cent.).

Other cyclic compounds of this type are included in Table III.

Lactones.

β-Salicyl-levulinic lactone.—Dry hydrochloric acid gas is passed into a mixture of levulinic acid (5 g.) and salicylaldehyde (5 g.) for about half an hour and the whole is allowed to stand overnight, when it solidifies *en masse*. The solid is washed with water, very dilute alcohol and ether and finally crystallised from hot alcohol. The reddish-violet micro-crystals, m.p. 151°, are soluble in alcohol, acetone but insoluble in ether, benzene, chloroform, etc., unaffected with cold sodium bicarbonate solution though soluble in hot bicarbonate or cold caustic soda (yield almost quantitative). (Found: C, 71·01; H, 4·45. $C_{12}H_{10}O_3$ requires C, 71·28; H, 4·89 per cent.).

A *monophenylhydrazone*, melting at 132°, is prepared in the usual manner. (Found: N, 9·37. $C_{18}H_{16}O_2N_2$ requiree N, 9·59 per cent.).

A *bromo-derivative* is prepared in the usual manner; pinkish needles melting at 128°. (Found: Br, 44·32. $C_{12}H_{10}O_3Br_2$ requires Br, 44·19 per cent.).

Other lactones are listed in Table IV.

TABLE I.

Open-chain Compounds.

Name.	Formula.	Method of preparation.	M.p.	Analysies. Calculated. %	Found. %	Properties.
β-*p*-Nitrobenzylidene-levulinic acid.	$NO_2C_6H_4\cdot CH=C(Ac)CH_2\cdot CO_2H$	*p*-Nitrobenzaldehyde + levulinic acid + dry HCl gas at 5°-10° for about half an hour (yield, 50%).	85°	N, 5·62	5·85	Orange needles from hot alcohol.
,, Phenylhydrazone	$C_{18}H_{17}O_4N_3$	Phenylhydrazine + the substance in acetic acid.	130°	N, 12·38	12·84	Yellow needles from alcohol.
,, Dibromo-derivative	$C_{18}H_{11}O_5NBr_2$	Alcoholic solution of the substance shaken with bromine water.	265°	Br, 39·12	38·99	Light yellow needles from hot dilute alcohol.
β-*p*-Nitrobenzylidene-δ-benzylidene levulinic acid	$NO_2C_6H_4\cdot CH=C(CO\cdot CH=CHPh)\cdot CH_2\cdot CO_2H$	β-*p*-Nitrobenzylidene-levulinic acid + benzaldehyde + 15% KOH (7·8 c.c.) on the water-bath for two hours (yield, 40%).	124°	N, 4·15	3·99	Yellow micro-crystalline powder. The identical compound is obtained from δ-benzylidine-levulinic acid + *p*-nitrobenzaldehyde + HCl gas.
β-*p*-Nitrobenzylidene-α-benzylidenelevulinic acid.	$NO_2C_6H_4\cdot CH=C(Ac)\cdot C(=CHPh)\cdot CO_2H$	Sodium salt of β-*p*-nitrobenzylidine levulinic acid + benzaldehyde + acetic anhydride on the water-bath for 20 hours (yield 55%).	260°	N, 4·15	3·74	Yellow needles from hot absolute alcohol.

δ-*p*-Nitrobenzylidene-levulinic acid	$NO_2C_6H_4\cdot CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	*p*-Nitrobenzaldehyde + levulinic acid + 15% NaOH on water-bath for two hours (yield, 30%).	240°	N, 5·62	5·32	Light orange plates from acetone.
,, Phenylhydrazone	$C_{17}H_{17}N_3O_4$	In the usual manner.	251°	N, 12·38	12·42	The hydrozane at once changes to a pyrazolone derivative (as it responds to Knorr's reaction.)
,, Dibromo-derivative	$C_{11}H_{11}O_5NBr_2$	,, ,,	269°	Br, 39·12	38·98	... ...
δ-*p*-Nitrobenzylidene-β-benzylidenelevulinic acid.	$NO_2C_6H_4\cdot CH=CH\cdot CO\cdot C(CH_2CO_2H)(CHPh)$	δ-*p*-Nitrobenzylidene levulinic acid + benzaldehyde + dry HCl gas (yield, 30-40%).	167°	N, 4·15	3·88	Light red plates from acetone.
δ-*m*-Nitrobenzylidene-levulinic acid.	$NO_2C_6H_4\cdot CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	*m*-Nitrobenzaldehyde + levulinic acid + 15% NaOH (yield, 40%)	254°	N, 5·62	5·51	Yellow powder; decolourises bromine.
,, Hydrazone	$C_{17}H_{17}N_3O_4$	In the usual manner	—	N, 12·38	12·21	Yellow powder.
,, Bromo-derivative	$C_{11}H_{11}O_5NBr_2$	,, ,,	—	Br, 39·12	38·88	Red powder.
Indigo		*o*-Nitrobenzaldehyde + levulinic acid + 15-20% NaOH	—	N, 10·67	10·74	Yield is only 5%.
δ-*o*-Nitrobenzylidene-levulinic acid.	$NO_2C_6H_4\cdot CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	,, (yield, 30%)	169°	N, 5·62	5·11	Light red powder (constitution under investigation). Does not give indigo on treatment with alkali.

TABLE I.—*continued*.

Name.	Formula.	Method of preparation.	M.p.	Analyses. Calculated.	Found.	Properties.
δ-*o*-Nitrobenzylidene-levulinic acid.	$NO_2C_6H_4\cdot CH=C(COCH_3)\cdot CH_2CO_2H$	*o*-Nitrobenzaldehyde + levulinic acid + dryHCl gas (yield, 60%)	121°	N, 5·62	5·46	Grey micro-crystals from alcohol; decolorises bromine water; gives a hydrazone (m.p. 92°).
β-*o*-Nitrobenzylidene-δ-benzylidenelevulinic acid	$NO_2C_6H_4\cdot CH=C(CO\cdot CH=CHPh)\cdot CH_2CO_2H$	In the usual manner (yield, 40%)	157°	N, 4·15	4·14	Yellow micro-crystalline powder from acetone.
δ-Cinnamyl-levulinic acid.	$C_6H_5CH=C(CO\cdot CH_3)\cdot CH_2CO_2H$	Cinnamic aldehyde + levulinic acid + dryHCl gas (yield, 80%)	115°	C, 73·04 H, 6·09	73·90 5·97	Orange plates from hot alcohol.
,, Dibromo-derivative (according to Thiele's theory)	$C_{14}H_{14}O_3Br_2$	In the usual manner.	—	Br, 41·03	41·02	Light yellow plates.
,, Phenylhydrazone	$C_{20}H_{20}O_2N_2$	,, ,,	136°	N, 8·75	8·53	Light red needles from alcohol.

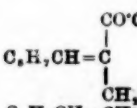
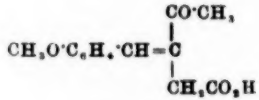
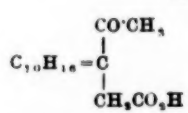
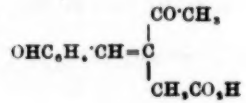
β-Cinnamyl-δ-benzylidenelevulinic acid		,, (yield 40%)	,,	112°	C, 79·24 H, 5·88	79·04 5·78	Yellow needles from acetone.
δ-Cinnamyl ,, ,,	$C_6H_5CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	Cinnamic aldehyde + levulinic acid + 15% NaOH (yield, 60%)		161°	C, 73·04 H, 6·09	72·68 6·07	Yellow needles; gives a hydrazone and decolorises bromine water.
β-Anisal ,, ,,		Anisaldehyde + levulinic acid + dry HCl gas (yield, 60%)		58°	C, 66·67 H, 5·99	66·02 5·52	Red needles from alcohol; reacts with phenylhydrazine; decolorises bromine water; very hygroscopic.
β-Citral ,, ,,		Citral + levulinic acid + dry HCl gas (yield, 25%)		187°	C, 67·42 H, 8·61	66·82 8·43	Orange-yellow powder from acetone.
δ-Vanillin ,, ,,	$(OH)(CH_3O)C_6H_3\cdot CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	Vanillin + levulinic acid + dilute NaOH (yield, 25-30%)		276°	C, 62·1 H, 5·6	61·51 5·37	Rose-red powder from alcohol; reacts with phenylhydrazine; decolourises bromine water.
δ-Salicyl ,, ,,	$(OH)C_6H_4\cdot CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	Salicylaldehyde + levulinic acid + dilute NaOH (yield 55%)		166°	C, 65·45 H, 5·45	64·96 5·28	Greyish brown powder; if however strong HCl is used to acidify, lactone is at once formed.
β-p-Hydroxybenzylidine levulinic acid		p-Hydroxybenzaldehyde + levulinic acid + dry HCl gas (yield 60%)		230°	C, 65·45 H, 5·45	65·05 5·41	Light red powder; reacts with phenylhydrazine, and decolorises bromine water.

TABLE I.—*Continued.*

Name.	Formula.	Method of preparation.	M.p.	Analyses. Calculated.	Found.	Properties.
δ-p-Hydroxybenzylidine levulinic acid	$OHC_6H_4\cdot CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	*p*-Hydroxybenzaldehyde + levulinic acid + dilute NaOH (yield, 25%)	109°	C, 65·45 H, 5·45	65·02 5·11	Yellow plates from hot dilute alcohol.
δ-m- ,, ,, ,,	$OHC_6H_4\cdot CH=CH\cdot CO\cdot CH_2CH_2CO_2H$	*m*-Hydroxybenzaldehyde + levulinic acid + dilute NaOH (yield, 30%)	110°	C, 65·45 H, 5·45	64·95 5·38	Dull red powder.
δ-Resorcylidenelevulinic acid	$(OH)_2C_6H_3\cdot CH=CH\cdot CO\cdot CH_2$ CH_2CO_2H	1 :2 :4-Resorcylaldehyde + levulinic acid + dilute NaOH (yield, 40%)	251°	C, 61·02 H, 5·08	61·07 5·11	Brown powder from hot alcohol; decolorises bromine and reacts with phenylhydrazine.

TABLE II.

Naphthalene Derivatives.

Name.	Formula.	Method of preparation.	M.p.	Analyses. Calculated.	Found.	Properties.
3-Aceto-6-(or 8)-nitro-1 naptbol.	I, NO_2 in 6 or 8 position	*m*-Nitrobenzaldehyde + levulinic + dry HCl gas at 0°—5° (yield 95%).	163°	N, 6·07	6·42	Red plates from acetone, insoluble in cold or hot Na-bicarbonate but soluble in NaOH.

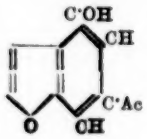
3-Aceto-5-nitro- ,, ,,	I, NO_2 in 5-position	*o*-Nitrobenzylidene-levulinic acid + acetic anhydride at 120-130° for 6 to 7 hours. (yield, 60%).	220°	N, 6·07	6·59	Brown micro-crystalline powder from acetone.
3-Aceto-7-methoxy ,,	I, OMe in 7-position	*β*-Anisal-levulinic acid + acetic anhydride at 140-145° for 4-5 hours (yield, 60%).	164°	C, 72·22 H, 5·55	71·96 5·42	Red powder soluble in caustic soda; insoluble in cold or hot bicarbonate; slight colouration with $FeCl_3$.
3-Aceto-7 :8 (or 6 :7)-dioxymethylene ,,	I, $O(CH_2)_2$: in 6 :7- or 7 :8-position.	Piperonal + levulinic acid + dry HCl gas at 0°-5° (yield, 50%).	234°	C, 67·83 H, 4·35	67·25 4·31	Flaky crystals of chocolate colour; insoluble in Na-bicarbonate soluble in NaOH; reacts with phenylhydrazine and benzaldehyde.
3-Aceto-7-hydroxy-8 (or 6)-methoxy-1-napthol	I, OH in 7, OMe in 6- or 8-position	Vanillin + levulinic acid + dry HOl gas at 5°-10°. (yield 60%)	169°	C, 67·23 H, 5·59	67·2 5·12	Reddish powder, soluble in NaOH; insoluble in Na-bicarbonate; reacts with phenylhydrazine.
3-Aceto-6(or 8)-hydroxy ,,	I, OH in 6 (or 8)-position	*m*-Hydroxybenzldehyde + levulinic acid + dry HCl gas at 0°-5°. (yield, 50%)	164°	C, 71·28 H, 4·89	70·83 4·61	Brown powder, insoluble in Na-bicarbonate but dissolves in NaOH; gives an oxime.
6-Aceto-4-oxycoumarone 		Furfuraldehyde + levulinic acid + dry HCl gas at 0°-5° (yield, 70%)	190°	C, 68·75 H, 4·54	67·92 4·52	Identical with Erdmann's compound.

TABLE III.

Benzo-cyclo-*octatetrene Derivatives.*

Name.	Formula.	Method of preparation.	M. p.	Analyses. Calculated.	Found.	Properties.
Benzo-9-nitro-1 :4-dihydroxy-*cyclo*-octatetrene	III, NO_2 in position 9	δ-*p*-Nitrobenzylidene-levulinic acid + acetic anhydride at about 140° for 3-4 hours.	210°	N, 6·07	6·41	Micro-crystalline powder from acetone; insoluble in $NaHCO_3$ (cold or hot), soluble in NaOH; reacts with phenylhydrazine; decolourises bromine; no reaction on $FeCl_3$.
Benzo-8(or 10)-nitro ,,	III, NO_2 in position 8 or 10	δ-*m*-Nitrobenzylidine-levulinic acid + acetic anhydride on water-bath for 5 hours.	296°	N, 6·07	6·39	Brown powder from acetone. Properties same as those of the preceding one.
Benzo-8-aceto-1-hydroxy ,,	III, H in place of OH in position 4 and $COCH_3$ in position 3.	β-Cinnamyl-levulinic acid + acetic anhydride at 130°-140° for about 4 hours.	230°	C, 79·24 H, 5·06	C, 78·86 H, 5·49	Red plates from acetone. Properties similar.
Benzo-9-methoxy-1 :4-dihydroxy- ,,	III, OMe in position 9.	δ-Anisal-levulinic acid + acetic anhydride for 4 to 5 hours.	78°	C, 72·22 H, 5·55	C, 72·01 H, 5·46	Red plates. Properties similar.
Benzo-9-hydroxy-1 :4-dihydroxy- ,,	III, OH in position 9.	δ-*p*-Hydroxybenzylidinelevulinic acid + acetic anhydride at 140° for 4-5 hours.	246°	C, 71·27 H, 4·89	C, 70·83 H, 4·43	Light red powder. Properties similar.

TABLE IV.

Lactones.

Name.	Formula.	Method of preparation.	M. p.	Analyses. Calculated.	Found.	Properties.
Cinnamylangelic lactone.	VI.	By heating δ-cinnamyllevulinic acid above its melting point.	Above 290°	C, 79·24 H, 5·66	78·5 5·62	Greyish-red powder; insoluble in cold $NaHCO_3$, dissolves when hot; does not give hydrazone.
β-Resorcyl-levulinic lactone.	$OH{\cdot}C_6H_3{\cdot}CH{=}C{\cdot}CO{\cdot}CH_3$ $O{-}CO{-}CH_3$	1 :2 :4-Resorcylaldehyde + levulinic acid + dry HCl gas (yield, 80%)	Above 210°	C, 66·06 H, 4·58	65·59 4·48	Bluish-violet powder; dyes silk a violet shade; insoluble in hot bicarbonate but not in the cold; reacts with $PhNHNH_2$.
δ-Salicylangelic lactone.	V.	On acidifying the Na-salt of δ-salicyl levulinic acid with conc. HCl (yield, 75%)	168°	C, 71·28 H, 4·89	70·94 4·68	Greyish-brown powder; gives coloration with $FeCl_3$; does not react $PhNHNH_2$; reacts with hot Na-bicarbonate
β-Napthyl-levulinic lactone.	$C_{10}H_6CH = C{\cdot}CO{\cdot}CH_3$ $O{-}CO{-}CH_2$	β-Hydroxynaphthyl aldehyde + levulinic acid + dry HCl gas (yield, 40%)	94°	C, 76·18 H, 4·38	75·31 4·5	Brown powder; insoluble in bicarbonate and in cold NaOH; dyes silk a brown shade, gives a bromo-derivative (m.p. 113°); benzylidene compound (m.p. 112°); reacts with $PhNH.NH_2$.

TABLE IV—*continued*.

Lactones.

Name.	Formula.	Method of preparation.	M. p.	Analyses. Calculated.	Found.	Properties.
Along with the above compound, another compound is formed in 20 p. c. yield.	Under investigation.		223°	C, 75·02 H, 4·76		Green powder; insoluble in caustic alkali; decolourises bromine water; does not give a hydrazone.
Glucoselevulinic lactone.	VII.	Glucose + levulinic acid dry HCl gas (yield, 20%)	96°	C, 50·77 H, 6·15	50·41 5·96	Red micro-crystalline powder; soluble in alcohol, acetone and chloroform; insoluble in cold bicarbonate soluble in caustic alkalis.
,, Tetra-acetyl derivative.		The above lactone + acetic anhydride on water-bath.	250°	C, 53·73 H, 5·67	52·95 5·27	A brown powder.

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The Influence of the Concentration of Coagulating Electrolyte, Time and Temperature on the Syneresis of some Inorganic Jellies.

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In previous communications (*Z. anorg. Chem.*, 1926, **152**, 399; 1927, **164**, 63; 1927, **168**, 209) from these laboratories, it has been mentioned that stable jellies of ceric hydroxide, vanadium pentoxide and silicic acid undergo syneresis in course of time due to the decrease in the hydration tendency of the particles forming the jelly. The syneresis in a blood clot (*J. Phys.Chem.*, 1929, **33**, 459) has also been considered as a parallel case. Holmes, Kaufmann and Nicholas (*J. Amer. Chem. Soc.*, 1919, **41**, 1329), Mukoyama (*Kolloid Z.*, 1927, **42**, 79), Fischer (*Koll.-Chem. Beih*, 1922, **15**, 3), Liepatov (*Kolloid Z.*, 1927, **41**, 200), Kunitz (*J. Gen. Physiol.*, 1928, **12**, 289), Kuhn (*Kolloid Z.*, 1928, **46**, 299), Arsem (*J. Phys. Chem.*, 1926, **30**, 306), and Hardy (*Proc. Roy. Soc.*, 1926, **112**, 47) are the other investigators who have studied the phenomenon of syneresis in the case of silicic acid, viscose, soap jellies, dyestuffs, gelatine and other organic jellies. Very little work seems to have been done on the syneresis of inorganic jellies. In the present communication, we have studied the influences of the concentration of the coagulating electrolytes, of time, and of temperature on the syneresis of the following jellies:

Ponceaux red, ferric phosphate, ferric arsenate, chromium arsenate, vanadium pentoxide, zirconium hydroxide, zirconium borate, ferric borate and manganese dioxide.

A. *Influence of Concentration of Coagulating Electrolytes and Time on Syneresis.*

A known amount of the jelly-forming substance was taken in 50 c.c. Jena-glass conical flasks, and to it varying amounts of electrolytes of concentrations suitable for the formation of the jellies were added. The same total volume was made up by the addition of the requisite amount of water. The conical flasks were well corked and then sealed with wax in order to prevent the evaporation of water. The jellies were allowed to stand for a day or so and then the synerised

liquid was carefully poured in a measuring tube graduated to one-tenth of a cubic centimeter. The volume could be read up to 0·05 c.c. The readings were reproducible and quite comparative, and consequently the amount of syneresis was determined. In order to find out the influence of time, a similar set of jellies was allowed to stand for 90 minutes, and the syneresis during this period was compared with that obtained when allowed to stand for a day or so.

Ponceaux Red Jelly.

Varying amounts of $N/10$-barium chloride solution were added to 10 c.c. of 2·5% Ponceaux red. The total volume was made up to 20 c.c. in each case. The jellies were allowed to stand for 46 hours and the synerised liquid was then carefully measured.

TABLE I.

2·5% Ponceaux red solution taken = 10 c.c.

$N/10$. $BaCl_2$.	Total volume.	Synerised liquid in c.c.		Percentage of syneresis.		Syneresis in 46 hrs. / $BaCl_2$.
		90 mins.	46 hrs.	90 mins.	46 hrs.	
8·5 c.c.	20 c.c.	—	0·95	—	4·75	0·112
9·0	20	0·1	1·20	0·5	6·00	0·133
9·5	20	0·2	1·50	1·0	7·50	0·158
10·0	20	0·45	2·30	2·25	11·5	0·230
11·0	21	—	2·60	—	12·4	0·236

It will be seen that the percentage of syneresis as well as the ratio between the amounts of syneresis and of coagulating electrolyte are increasing with the increase in the concentration of the electrolyte.

Ferric Phosphate Jelly.

The sol of ferric phosphate was prepared by adding potassium phosphate to ferric chloride solution in slight excess and dialysing the mixture for 11 days. The sol contained 54·74 g. of ferric phosphate per litre. To 10 c.c. of the sol taken in Jena flasks varying ing amounts of $N/5$-potassium sulphate solution were added. The

jellies were allowed to stand for 22 hours, and the amount of synerised liquid was measured.

TABLE II.

Sol taken each time = 10 c.c. Total volume = 20 c.c.

$N/5$-K_2SO_4.	Synerised liquid in c.c. 90 mins.	22 hrs.	Percentage of syneresis. 90 mins.	22 hrs.	Syneresis in 22 hrs. / K_2SO_4
2·0 c.c.	—	0	—	0	0
3·0	0·65	1·05	3·25	5·25	0·35
4·0	1·05	1·55	5·25	7·75	0·39
5·0	2·0	2·20	10·0	11·1	0·44
10·0	Precipitated.				

The percentage of syneresis and the ratio between the amount of syneresis and the concentration of the electrolyte increase as the concentration of the electrolyte increases.

Ferric Arsenate Jelly.

The sol of ferric arsenate was obtained by adding potassium arsenate solution to a ferric chloride solution till the precipitate formed just dissolved on shaking. The mixture was dialysed for 7 days. It contained 31·72 g. of ferric arsenate per litre. 10 C.c. of the sol were mixed with different amounts of normal potassium sulphate. The jellies were allowed to stand for 24 hours.

TABLE III.

Sol taken each time = 10 c.c. Total volume = 12 c.c.

N-K_2SO_4.	Synerised liquid in c.c. 90 mins.	24 hrs.	Percentage of syneresis. 90 mins.	24 hrs.	Syneresis in 24 hrs. / K_2SO_4.
0·2 c.c.	—	0	—	0	0
0·3	0·2	1·15	1·67	9·58	3·83
0·4	1·1	1·50	9·17	12·50	3·75
0·5	1·4	1·70	11·67	14·17	3·40
0·7	—	1·95	—	16·25	2·80

The percentage amount of syneresis increases with the increase in the concentration of the coagulating electrolyte, whilst the ratio between the amount of syneresis and the electrolyte approaches a maximum and then decreases with the increase in the concentration of the coagulating electrolyte.

Chromium Arsenate Jelly.

The sol was obtained by adding potassium arsenate to chromic chloride solution in slight excess and dialysing the mixture for 5 days. The concentration of the sol was 57·6 g. chromium arsenate per litre. To 10 c.c. of the sol were added different amounts of normal potassium sulphate and the total volume was made up to 12 c.c. in every case. The jellies were allowed to stand for 24 hours before the syneresis was measured.

TABLE IV.

Sol taken each time = 10 c.c. Total volume = 12 c.c.

N-K_2SO_4.	Syneresed liquid in c.c.		Percentage of syneresis.		Syneresis in 24 hrs.
	90 mins.	24 hrs.	90 mins.	24 hrs.	$\frac{}{K_2SO_4}$.
0·2 c.c.	—	0	—	0	0
0·3	—	0·2	—	1·66	0·66
0·4	—	0·4	—	3·33	1·00
0·5	0·10	0·5	0·82	4·17	1·00
0·7	0·25	0·5	2·08	4·17	0·71
0·9	0·25	0·5	2·08	4·17	0·71
1·0	—	0·5	—	4·17	0·50

The amount of syneresis appears to increase with the increase in the concentration of the coagulating electrolyte. The ratio between the amount of syneresis and the electrolyte reaches a maximum and then decreases.

Vanadium Pentoxide Jelly.

Vanadic acid was precipitated by the addition of concentrated hydrochloric acid to ammonium vanadate, and it was suspended in

water and dialysed for 5 days. The sol contained 4·62 g. of V_2O_5 per litre. To 10 c.c. of the sol, were added varying amounts of normal potassium chloride, and the jellies were allowed to stand for 22 hours before the amount of syneresis was measured.

TABLE V.

Sol taken each time = 10 c.c. Total volume = 12 c.c.

N-KCl.	Synerised liquid in c.c. 90 mins.	22 hrs.	Percentage of syneresis. 90 mins.	22 hrs.	Syneresis. in 22 hrs. KCl.
0·3 c.c.	—	0·45	—	3·75	1·50
0·5	—	0·70	—	5·83	1·40
0·7	0·4	0·95	3·33	7·91	1·35
0·9	0·5	1·10	4·17	9·17	1·20
1·1	1·7	1·30	5·83	10·83	1·18

The amount of syneresis increases and the ratio between the amount of syneresis and the concentration of the electrolyte decreases with the increase in the concentration of the coagulating electrolyte.

Zirconium Hydroxide Jelly.

The sol was prepared by dialysing a 10 per cent. solution of zirconium nitrate for 7 days. The concentration of the sol was 37·42 g. of ZrO_2 per litre. To 10 c.c. of the sol were added varying amounts of *N*/5-potassium sulphate and the jellies were allowed to stand for 26 hours before the syneresis was measured.

TABLE VI.

Sol taken each time = 10 c.c. Total volume = 15 c.c.

N/5-K_2SO_4.	Synerised liquid in c.c. 90 mins.	26 hrs.	Percentage of syneresis. 90 mins.	26 hrs.	Syneresis in 26 hrs. K_2SO_4.
3·5 c.c.	Not set	0	Not set	0	0
4·0	0	0·6	0	4·0	0·15
4·5	0·05	0·9	0·33	6·0	0·20

The percentage of syneresis and the ratio between the amount of syneresis and the concentration of the coagulating electrolyte increase with the concentration of the electrolyte.

Zirconium Molybdate Jelly.

The sol was prepared by dialysing a mixture of potassium molybdate and zirconium nitrate in excess for 4 days. The concentration of the sol was 45·2 g. of zirconium molybdate per litre. To 10 c.c. of the sol were added varying amounts of $N/5$-potassium sulphate and the jellies were allowed to stand for 24 hours before the synerised liquid was measured.

TABLE VII.

Sol taken each time = 10 c.c. Total volume = 12 c.c.

$N/5$-K_2SO_4.	Synerised liquid in c.c.		Percentage of syneresis.		Syneresis in 24 hrs.
	90 mins.	24 hrs.	90 mins.	24 hrs.	K_2SO_4
0·5 c.c.	—	0	—	0	0
0·8	—	0	—	0	0
1·0	0	0·1	0	0·83	0·10
1·5	0·2	1·2	1·66	10·0	0·80
2·0	0·9	2·0	7·5	16·6	1·00

The percentage of the syneresis, as well as the ratio between the syneresis and the coagulating electrolyte increase as the concentration of the electrolyte increases.

Zirconium Borate Jelly.

The jelly was prepared by dialysing a mixture of zirconium nitrate and borax solutions. The concentration of the sol was 14·84 g. of zirconium borate per litre. It was dialysed for 8 days. To 10 c.c. of the sol were added varying amounts of $N/5$-potassium sulphate solution, and the jellies were allowed to stand for 24 hours before the syneresis was measured.

TABLE VIII.

Sol taken each time = 10 c.c. Total volume = 11·8 c.c.

N/5-K_2SO_4.	Synerised liquid in c.c.	Percentage of syneresis.	Syneresis / K_2SO_4.
1·2 c.c.	1·7	14·4	1·41
1·4	2·5	21·2	1·78
1·6	2·85	24·1	1·78
1·8	3·20	27·1	1·77

It will be seen from the table that the syneresis increases with the increase in the concentration of the electrolyte, whereas the ratio between the two attains a maximum value and then decreases. The influence of time on syneresis is shown in the following table.

TABLE IX.

Sol taken each time = 10 c.c. Total volume = 11·2 c.c.

N/5-K_2SO_4.	Syneresis after 90 mins.	Syneresis after 24 hrs.
0·8 c.c.	0 c.c. = 0%	0·3 c.c. = 2·68%
1·0	0 = 0	1·3 = 11·6
1·2	0·4 = 3·57	2·0 = 17·8

Ferric Borate Jelly.

A sol was obtained by dialysing a mixture of borax and ferric chloride solution in excess for 30 days. The concentration of the sol was 32·48 g. of ferric borate per litre. To 10 c.c. of the sol were added varying amounts of normal potassium chloride and the jellies were allowed to stand for 24 hours before the synerised liquid was measured.

TABLE X.

Sol taken each time = 10 c.c. Total volume = 10·6 c.c.

N-KCl.	Synerised liquid in c.c.		Percentage of syneresis		Syneresis in 24 hrs. / K_2SO_4
	90 mins.	24 hrs.	90 mins.	24 hrs.	
0·2 c.c.	—	0·15	—	1·41	0·75
0·3	—	0·40	—	3·78	1·33
0·4	0·2	0·70	1·9	6·60	1·75
0·5	0·3	0·75	2·83	7·09	1·50
0·6	0·35	0·80	3·3	7·55	1·36

The amount of syneresis increases as the concentration of the coagulating electrolyte increases but the ratio between the amount of syneresis and the electrolyte approaches a maximum and then decreases.

Manganese Dioxide Jelly.

A 25 per cent. solution of glucose and a 10 per cent. caustic soda solution (2·566*N*) were prepared. To 2 c.c. of the glucose solution, 1 c.c. of caustic soda was added and varying amounts of 14 per cent. potassium permanganate solution (1·66*N*) were gradually added with constant stirring, and the mixture was all along cooled in ice. When the jelly was formed, it was allowed to stand for 90 minutes and then the synerised liquid was measured.

TABLE XI.

Caustic soda solution (2·566*N*) added each time = 1 c.c.
Total volume = 20 c.c.

25% Glucose.	14% $KMnO_4$.	Synerised liquid in c.c.		Percentage of syneresis.		Syneresis in 90 min. / $KMnO_4$.
		90 mins.	2 days.	90 mins.	2 days.	
2 c.c.	14 c.c.	1·1	—	5·5	—	0·078
2	15	1·3	3·7	6·5	18·5	0·087
2	16	1·85	4·4	9·25	22·0	0·116
2	17	2·8	4·8	14·0	24·0	0·165
3	16	0·9	—	4·5	—	0·056

The amount of syneresis increases as the amount of potassium permanganate increases and the ratio between the amount of syneresis and permanganate also increases. The addition of more glucose decreases the amount of syneresis.

B. *The Influence of Temperature on Syneresis.*

A known amount of sol was taken in 50 c.c. Jena flasks and mixed with different amounts of electrolytes and the volume was kept constant in every case. The flasks were well corked and allowed to stand in thermostats maintained at constant temperatures. Three sets of every jelly were prepared and one of them was allowed to

stand at the temperature of 30° and the other two at temperatures of 50° and 70° respectively. The jellies were kept at these temperatures for 90 minutes in every case. After this the synerised liquid was poured in a graduated measuring tube, and the amount of syneresis at different temperatures was thus measured.

The results obtained are recorded in the following tables. The values given in the column of temperature coefficients denote the increase in the amount of syneresis per 10° rise in temperature.

Ponceaux Red Jelly.

2·5 per cent. solution of the dyestuff taken each time = 10 c.c.
Total volume = 20 c.c. Time given = 90 minutes.

TABLE XII.

N/10-$BaCl_2$.	Amount of syneresis at			Temperature coefficients between	
	30°	50°	70°	30° and 50°	50° and 70°.
9·0 c.c.	0·1	0·1	0·2	0	0·05
9·5	0·2	0·45	0·7	0·125	0·125
10·0	0·45	0·6	0·8	0·075	0·100

Ferric Phosphate Jelly.

The sol was dialysed for 11 days. Concentration = 54·74 g. ferric phosphate per litre.

Sol taken each time = 10 c.c. Total volume = 20 c.c. Time given = 90 minutes.

TABLE XIII.

N/5-K_2SO_4.	Amount of syneresis at			Temperature coefficients between	
	30°	50°	70°	30° and 50°	50° and 70°.
3 c.c.	0·65 c.c.	0·7 c.c.	1·15 c.c.	0·025	0·225
4	1·05	1·1	1·6	0·025	0·250
5	1·7	1·7	2·1	0·0	0·200

Ferric Arsenate Jelly.

The sol was dialysed for 7 days. Concentration = 31·72 g. ferric arsenate per litre.

Sol taken each time=10 c.c. Total volume=12 c.c. Time given=90 minutes.

TABLE XIV.

N-K_2SO_4.	Amount of syneresis at			Temperature coefficient between	
	30°	50°	70°	30° and 50°	50° and 70°.
0·3 c.c.	0·2 c.c.	0·6 c.c.	0·9 c.c.	0·20	0·15
0·5	1·1	1·2	1·35	0·05	0·075
0·7	1·4	1·5	1·8	0·05	0·150

Chromium Arsenate Jelly.

Dialysed for 5 days. Concentration of the sol=57·6 g. chromium arsenate per litre. Sol taken each time=10 c.c. Total volume=12 c.c. Time given =90 minutes.

TABLE XV.

N-K_2SO_4.	Amount of syneresis at			Temperature coefficient between	
	30°	50°	70°	30° and 50°	50° and 70°.
0·5 c.c.	0·1 c.c.	0·3 c.c.	0·35 cc.	0·1	0·025
0·7	0·3	0·4	0·5	0·05	0·05
0·9	0·3	0·4	0·5	0·05	0·05

Vanadium Pentoxide Jelly.

Dialysed for 5 days. Concentration of the sol=4·62 g. V_2O_5 per litre. Sol taken each time=10 c.c. Total volume=12 c.c. Time given =90 minutes.

TABLE XVI.

N-KCl.	Amount of syneresis at			Temperature coefficient between	
	30°	50°	70°	30° and 50°	50° and 70°.
0·7 c.c.	0·4 c.c.	0·4 c.c.	0·5 c.c.	0	0·05
0·9	0·5	0·6	0·7	0·05	0·05
1·1	0·7	0·75	0·85	0·025	0·05

Zirconium Hydroxide Jelly.

Dialysed for 7 days. Concentration of the sol=37·42 g. ZrO_2 per litre. Sol taken each time=10 c.c. Total volume=15 c.c. Time given =90 minutes.

TABLE XVII.

$N/5$-K_2SO_4.	Amount of syneresis at			Temperature coefficient between	
	30°	50°	70°	30° and 50°	50° and 70°.
3·5 c.c.	Not set	0·05 c.c.	0·6 c.c.	—	0·275
4·0	0 c.c.	0·1	·07	0·05	0·300
4·5	0·05	0·5	1·6	0·225	0·55

Zirconium Molybdate Jelly.

Dialysed for 4 days. Concentration of the sol=45·2 g. zirconium molybdate per litre. Sol taken each time=10 c.c. Total volume=12 c.c. Time given=90 minutes.

TABLE XVIII.

$N/5$-K_2SO_4.	Amount of syneresis at			Temperature coefficient between	
	30°	50°	70°	30° and 50°	50° and 70°.
1·0 c.c.	0 c.c.	0·1 c.c.	0·6 c.c.	0·05	0·25
1·5	0·2	0·6	1·8	0·20	0·60
2·0	0·9	1·9	3·2	0·50	0·65

Ferric Borate Jelly.

Dialysed for 30 days. Concentration of the sol=32·48 g. ferric borate per litre. Sol taken each time=10 c.c. Total volume=10·6 c.c. Time given=90 minutes.

TABLE XIX.

N-KCl.	Amount of syneresis at			Temperature coefficient between	
	30°	50°	70°	30° and 50°	50° and 70°.
0·4 c.c.	0·20 c.c.	0·20 c.c.	0·30 c.c.	0	0·05
0·5	0·30	0·30	0·35	0	0·035
0·6	0·35	0·40	0·45	0·025	0·025

Zirconium Borate Jelly.

Dialysed for 8 days. Concentration of the sol=14·84 g. zirconium borate per litre. Sol taken each time=10 c.c. Total volume=11·2 c.c. Time given=90 minutes.

TABLE XX.

N/5-K_2SO_4.	Amount of syneresis at			Temperature coefficient between	
	30°	50°	70°	30° and 50°	30° and 70°.
0·8 c.c.	0 c.c.	0·1 c.c.	0·6 c.c.	0·05	0·25
1·0	0	0·45	1·7	0·325	0·525
1·2	0·4	1·4	2·4	0·500	0·500

Manganese Dioxide Jelly.

25 per cent. glucose solution taken each time=2 c.c.

2·566*N*-Caustic soda added=1 c.c. Total volume=20 c.c.

Strength of potassium permanganate solution=1·66*N*

The jellies have been formed at 0°, and then transferred to baths maintained at 15° and 30°, and they were allowed to stand for 90 minutes before the syneresis was measured.

TABLE XXI.

$KMnO_4$	Amount of syneresis at		Temperature coefficient.
	15°	30°	
14 c.c.	1·1 c.c.	2·5 c.c.	0·93
15	1·3	2·8	4·00
16	1·85	2·9	0·7
17	2·8	3·2	0·27

The results recorded in the foregoing tables bring out the following facts:

Whenever a jelly is formed by the addition of coagulating electrolytes, (*a*) the amount of syneresis increases as the concentration of the electrolyte increases and (*b*) the ratio between the amount of syneresis and the concentration of the coagulating electrolyte either increases continually or tends to attain a maximum and then it diminishes with the concentration of the electrolyte. Thus the amount of syneresis does not increase in the same proportion as the coagulating electrolyte. The jellies of ferric arsenate, chromium arsenate, zirconium borate and ferric borate show the maximum clearly, whilst those of ponceaux red, ferric phosphate, zirconium hydroxide zirconium molybdate and manganese dioxide show the continuous increase in the ratio between the amount of syneresis and the concentration of the electrolyte as the concentration of the electrolyte increases.

Syneresis is likely to be due to a decrease in the hydration and it appears that on allowing some of the jellies to stand for some time, hydration tendency of the particles and the free surface become less and this causes the shrinkage of the network. It has been observed that the addition of an excess of electrolyte in coagulating the sol, accelerates the agglomeration of the particles and diminishes the hydration. Thus shortly after setting of the jelly, the excess of the electrolyte brings about the syneresis, and if the electrolyte is in large excess, the jelly will not set at all but a gelatinous precipitate will be obtained. Thus on increasing the concentration of the coagulating electrolyte, the following may happen (Prakash and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 408).

(*i*) Up to a limit—no jelly formation;

(*ii*) Up to the second limit—stable jellies undergoing no appreciable syneresis;

(*iii*) Between the second and third limits—firm jellies readily synerising;

(*iv*) Above the third limit—no jelly formation but a gelatinous precipitate is obtained.

Between the second and third limits, the phenomenon of syneresis is observed. In this limit, the increase in the concentration of the electrolyte always increases the amount of syneresis. The ratio between the amount of syneresis and the concentration

of the electrolyte sometimes increases continuously and sometimes attains a maximum as the concentration of the electrolyte is increased.

It has been observed that the syneresis starts a short time after the setting of the jelly, and the amount of syneresis increases as the time advances. After a certain time, the rate of the increase of syneresis diminishes and then syneresis stops. On allowing the jelly to stand further, no marked difference in the amount of syneresis will be observed. It has been seen that in the inorganic jellies investigated, this stage is attained in about two days. The increment in the percentage of the syneresis at two different intervals of time, sometimes diminishes with the concentration of the electrolyte (as in the case of ferric arsenate, chromium arsenate, and ferric borate jellies), sometimes increases (as in the cases of ponceaux red, zirconium hydroxide, zirconium molybdate and zirconium borate) and sometimes attains a maximum (as in the case of ferric phosphate, vanadium pentoxide and manganese dioxide) and as such no definite relationship between electrolyte-effect and time-effect has been observed. It appears that in most cases, the time-effect will either increase or attain a maximum with the increase in the concentration of the electrolyte.

The temperature-effect on the syneresis of many jellies has also been studied. It has been observed that the amount of syneresis is markedly increased at higher temperatures. Syneresis at three temperatures (30°, 50° and 70°) has been investigated, and it is found that the temperature coefficient between 30° and 50° is much less in all cases than between 50° and 70°.

Some of the jellies have almost no tendency towards syneresis. The jellies of thorium arsenate, phosphate and molybdate, and the jellies of iron, chromium and aluminium hydroxides do not undergo any syneresis even when kept for a long time. The syneresis has also been observed in the jellies of stannic hydroxide, borate and tungstate.

Arsem (*J. Phys. Chem.*, 1926, **30**, 306) advances the view that structural arrangement of units in a gel is inherently unstable, and he supposes that a further condensation of the associated phase is possible through three agencies: the re-orientation of units, the release of loosely combined molecules of the liquid phase and the union of previously non-functioning residual valencies. Wherever, there is a complete re-orientation of the structural units of a gel,

it reverts to a mixture of crystals and free liquid. According to him, the syneresis is due to the shrinkage of solid phase caused by progressive association and re-orientation of molecular units.

In a previous communication (*loc.cit.*), we have shown that the nature of a jelly is determined by two factors: the hydration tendency of the particles, and secondly the agglomeration tendency; and when the hydration tendency predominates over the agglomeration tendency, the jellies obtained are comparatively more transparent and stable and there is less possibility of the shrinkage of the network, and such jellies do not synerise to an appreciable extent. But whenever there is a diminution in hydration and increase in the agglomeration, the jellies are opaque and their stability is also diminished; and with more and more of the agglomeration, the possibility of the shrinkage of the jelly structure becomes greater, and then the jelly either partially gives up the liquid phase or is completely precipitated. The re-orientation of the molecular units to account for the syneresis in a jelly, does not appear to be essential and probable and the whole phenomenon of syneresis can be easily explained on the hydration and agglomeration hypothesis. Our results on the influence of the concentration of electrolytes on the amount of syneresis are in agreement with it. We have found that as the concentration of the electrolytes is increased, the amount of syneresis is also increased. The addition of coagulating electrolyte to a jelly-forming sol diminishes the charge on the colloidal particles, and the hydration is increased till a jelly is obtained, and by adding a further amount of electrolyte, the same forces which bring about the hydration, cause the particles to agglomerate, and the structure of the jelly undergoes a shrinkage. The increment in the temperature is also favourable for agglomeration and as such we have found that at higher temperatures, there is more syneresis in jellies.

Hardy (*Proc. Roy. Soc.*, 1926, **112**, 59) has studied the relation of syneresis to the freezing of the gel which he accounts on the basis of hydration and dehydration of the particles. He regards the swelling of gelatine as negative syneresis.

Most of the inorganic jellies investigated do not completely synerise even after the interval of several days, and had the re-orientation of the molecular units, as Arsem (*loc. cit.*) thinks, been the only cause of the syneresis, the amount of syneresis would have been continuously increased, as the ageing is increased, for, there

is no reason why re-orientation should stop after a time till it is not complete. From our results we have shown that the amount of the coagulating electrolyte added to a jelly controls the extent of syneresis. There is always a fixed minimum of the amount of the electrolyte necessary to give a permanent jelly, and any amount greater than that will cause syneresis. The greater the excess of the electrolyte over this fixed minimum, the greater will be the syneresis. The extent to which this syneresis will proceed will always depend upon the excessive electrolyte, and as such with a definite amount of electrolyte, the jelly is never completely synerised.

According to von Weimarn (*Rep. Imp. Ind. Res. Inst. Osaka*, 1928, **9**, 1) the total amount of water imbibed in a jelly is supposed to consist of (*i*) interatomic hydration, *e.g.*, water in crystal hydrates, (*ii*) 'surface hydration' and (*iii*) 'structure hydration' *i.e.*, water enclosed by the pores of the structural elements of the jelly. No quantitative data appear to be available as regards the interatomic hydration of these jellies, of which even the crystalline nature is doubtful; and yet, if some liquid exists in this state, it does not influence much the nature of a jelly. Surface hydration is the prime factor in the process of gelation and we have emphasised that this originates from gradual and regular charge neutralisation of hydrophile colloids by suitable electrolytes present. When hydration has reached a maximum stage, jelly elements are formed. These elements then, owing to their residual forces which would have otherwise brought about the agglomeration, imbibe the whole of the remaining solvent and give a solid jelly.

The process of syneresis is accompanied by the squeezing out of the liquid and shrinkage of the solid mass. Even in those jellies, which synerise to a great extent like blood clot or vanadium pentoxide, the whole of the solvent is never squeezed out, and the solid mass remaining after the maximum syneresis is still gelatinous in nature. This goes to show that the particles are still hydrated. When a jelly has been formed, the excess of the coagulating electrolyte tends to bring about the agglomeration and dehydration of the particles. This agglomeration tendency is the cause of the shrinkage of the solid mass. When particles have been slightly dehydrated, the 'structurally' imbibed water become loosened and comes out as the synerised product. Thus the synerised liquid appears to be mostly the liquid caught in the network of the jelly and partly formed by the dehydration of the particles.

Some jellies break up completely but do not show ordinary syneresis. The case of the true syneresis should be distinguished from that of the breaking up of a jelly. In the case of truely syneris-ed bodies, the mass remaining after the maximum syneresis is still much hydrated, but in the other case, the jelly leads to a justly dehydrated powder settling to the bottom. Most of the von Weimarn jellies, after a few hours (and some after a few days) leave, only the precipitated dehydrated mass and the separated solvent. This may be called the breaking up of a jelly, and not the true syneresis. Here the agglomeration and dehydration tendency is so great that the jellies are unstable and the solid precipitates out after a short time. Similar is the case with the manganese dioxide jelly prepared by Weitzemann's method (*J. Amer. Chem. Soc.*, 1915, **37**, 1082; 1917, **39**, 27). An interesting case has been observed with thorium molybdate jellies. Most of these jellies are very stable and do not undergo any syneresis (*J. Indian Chem. Soc.*, 1929, **6**, 590), but some of these jellies which have been prepared by the use of a large amount of potassium molybdate, precipitate out without undergoing any proper syneresis after ten or twelve days. This precipitation is due to the marked dehydration of the superficially hydrated jelly-elements and is brought about by the excess of the potassium molyb-date present. Thus, in true syneresis, the jelly elements are never completely dehydrated,and it is mainly the structurally imbibed liquid which is squeezed out. In the case of precipitation or breaking up of the jelly, dehydration of the elements appears practically complete.

Usher (*Proc. Roy. Soc.*, 1929, **A125**, 143) claims to have been successful in gelatinising such lyophobic substances as cadmium sulphide and gamboge in presence of suitable concentrations of sodium chloride. He assumes that whenever the solid framework of a rigid two-phase system becomes thickened in consequence of internal packing, the system becomes physically heterogeneous and hence undergoes syneresis. However, this explanation does not appear to be adequate in view of the fact that even dilute jellies where internal packing is not so dense, undergo marked syneresis, and some of the concentrated jellies also do not synerise.

Summary.

1. The influence of the concentration of coagulating electrolytes, time and temperature on the syneresis of the following jellies has been investigated:

Ponceaux red, ferric arsenate, ferric phosphate, ferric borate, chromium arsenate, vanadium pentoxide, zirconium hydroxide, zirconium molybdate, zirconium borate, and manganese dioxide.

2. It has been found that whenever a jelly is formed by the addition of electrolytes to a jelly-forming sol, the amount of syneresis increases continuously with the concentration of the electrolyte and the ratio between the amount of syneresis and the concentration of the electrolyte either increases or attains a maximum with the increase in the concentration of the electrolyte.

3. The amount of syneresis increases with time in the beginning but further syneresis stops after an interval. In the jellies investigated, the maximum syneresis is obtained within two days.

4. It has been observed that the amount of syneresis in the above jellies is greater at higher temperatures. The temperature coefficient of syneresis between 50° and 70° is invariably higher than that between 30° and 50°.

5. The phenomenon of syneresis has been explained on the hydration and agglomeration hypotheses of the jelly-forming particles. It has been advanced that the amount of coagulating electrolytes added to a jelly-forming sol controls not only the nature of the jelly, but also the extent of syneresis. There is always a fixed minimum of the amount of the coagulating electrolyte necessary to give a stable jelly, and any amount greater than that will bring about the syneresis. The addition of large amounts of electrolytes gives only a gelatinous precipitate, and not a jelly, because in that case, the agglomeration tendency of the particles predominates over the hydration tendency.

6. The true syneresis is quite distinct from that of the breaking up of a jelly. In true syneresis, the particles even after the maximum syneresis remain hydrated and gelatinous, while in the other case, a precipitated dehydrated mass is obtained. It is mainly the structurally imbibed liquid which is squeezed out during the true syneresis.

7. The idea that syneresis is due to the re-orientation of the particles appears to be inadequate, and similarly the view that this phenomenon is due to the heterogeneity produced by the intense internal packing of the particles also appears to be unsatisfactory.

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Formation of Heterocyclic Compounds. Part VI. Synthesis of Tetrahydroacridones.

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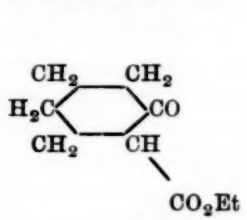
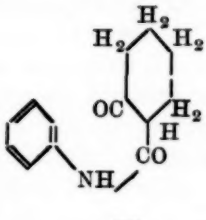
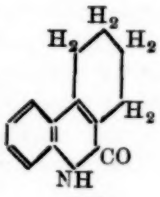
In a previous paper (*J. Indian Chem. Soc.*, 1929, **6**, 309), it was shown that by boiling a mixture of ethyl *cyclo*hexanone-2-carboxylate (I) and an arylamine for a few minutes, *cyclo*hexanone-2-carbanilide (II) is produced, which in its turn on treatment with concentrated sulphuric acid on the water-bath, may be easily converted into a tetrahydrophenanthridone derivative (III). It was also pointed out in that communication that by conducting the same reaction at the ordinary temperature, an anil (IV) could be readily obtained. This has been now fully realised as several primary aromatic amines have been condensed with ethyl *cyclo*hexanone-2-carboxylate and the reaction product have been further induced to undergo an intramolecular condensation to give rise to different tetrahydroacridone derivatives (V).*



(I)



(II)



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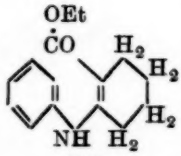

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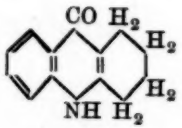
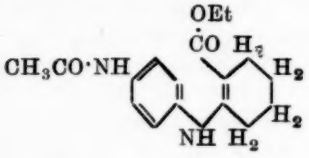


(V)

* Although published in May, 1929, there is no reference to this communication in a paper communicated by Blount, Perkin and Plant on the 29th June, 1929, and published in the Journal of London Chemical Society, in September, 1929. This oversight might have been due to the latter authors not having noticed our aforesaid communication.

Aniline, *p*-toluidine, and *m*-xylidine readlily react with ethyl *cyclo*hexanone-2-carboxylate at the room temperature to give rise to different anils and these on being heated for a short time at 260-265° yielded the corresponding tetrahydroacridone derivatives. It is only in the former case that the anil was obtained in a pure state, but other anils remained as a reddish-brown oil which resisted all attempts to solidify them. *p*-Aminoacetanilide also yields an anil, ethyl 2-*p*-acetaminoanilido*cyclo*hexane-1-carboxylate, but this cannot be induced to undergo intramolecular condensation either by heating or by the action of concentrated sulphuric acid. The sulphuric acid solution on dilution gives diazo-reaction and the non-formation of any acridone derivative may by accounted for by the presence of the anil (VI) in the form of an ion (VII) in concentrated sulphuric acid solution (*cf.* Roberts and Turner, *J. Chem. Soc.*, 1927, p. 1832). The ease of all such condensations appears to be affected mostly by the basicity of the amine used, for no nitraniline, or β-naphthylamine could be made to condense with the ester.



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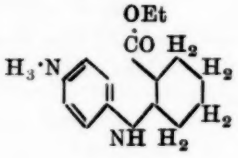

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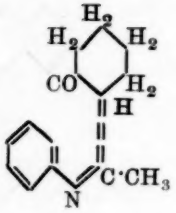

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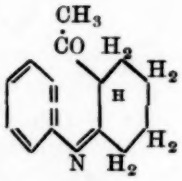


(IX)

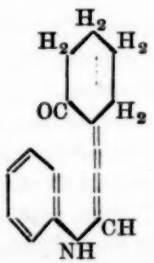
Kötz and Merkel (*J. pr. Chem.*, 1909, **79**, 122) obtained ethyl 2-anilido-$\triangle^{1:2}$-*cyclo*hexene-1-carboxylate (IV) by heating a mixture of ethyl *cyclo*hexanone-2-carboxylyte with aniline and keeping the product for several days. But it has already been shown (Sen and

Basu, *loc. cit.*) that this kind of reaction gives rise to *cyclo*hexanone-2-carbanilide (m.p. 105°) (II). That the Kötz and Merkel's compound is an anil is further evident from the fact that it readily yields 1:2:3:4-tetrahydroacridone (V), the constitution of which is known as it can be synthesised by heating a mixture of *cyclo*hexanone and anthranilic acid (Tiedtke, *Ber.*, 1909, **42**, 631).

All the tetrahydroacridone derivatives described in this paper are well crystalline solids of high melting points. They are soluble in most organic solvents and are more basic than their isomeric tetrahydrophenanthridone derivatives as they easily dissolve even in dilute acids.

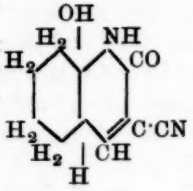
It is curious to note that whilst (II), (IV), (VIII) and (IX)—the two latter obtained by the action of aniline on 2-acetyl*cyclo*hexanone (Borsche, *Annalen*, 1910, **317**, 70), can be readily dehydrated to yield ring-compounds, the analogous compound (X*a* or X*b*) obtained by the action of aniline on 2-hydroxymethylene*cyclo*hexanone cannot be induced to undergo an intramolecular condensation. This behaviour of 2-hydroxymethylene*cyclo*hexanone derivative also suggest that its constitution would be best represented by (X*a*) as previously mentioned (Sen and Basu, *loc. cit.*).

Inactivity of this compound led us to study the action of ammonia on 2-hydroxymethylene *cyclo*hexanone. The amide (m.p. 112°) obtained by the action of liquor ammonia on 2-hydroxymethylene-*cyclo*hexanone readily reacts with excess of hydroxylamine hydrocloride to give rise to the oxime of 2-cyano*cyclo*hexanone evidently by the intermediate formation of the *iso*oxazole derivative (Auwers, Bohr and Fresse, *Annalen*, 1925, **414**, 68). The amide also reacts with cyanoacetamide to give rise to the quinoline derivative (XI, Sen-Gupta *J. Chem. Soc.*, 1915, **107**, 1351).

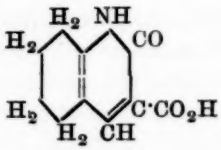


(X*a*)

(X*b*)



(XI)



(XII)

which in its turn can be hydrolysed with concentrated sulphuric acid to the acid (XII).

Experimental.

Ethyl cyclo*Hexanone-2-carboxylate and Aniline.*: (*i*) *Formation of Ethyl 2-Anilido-*$\triangle^1$*-cyclohexene-1-carboxylate* (IV).—Ethyl *cyclo*hexanone-2-carboxylate (4 g.) and aniline (2·2 g.) were mixed together in a small flask and left overnight in vacuum over fused calcium chloride. After three days fine crystals began to separate and in a week the contents in the flask set in to a crystalline solid (yield, 5 g.), which was collected and dried over porous plate. (Found: N, 5·91. $C_{15}H_{19}O_2N$ requires N, 5·71 per cent.).

The substance crystallises from methyl alcohol in very light yellow prisms and melts at 58·5°. It is soluble in ether, alcohol, and even in petroleum ether in which the corresponding anilide (*cyclo*hexanone-2-carboxylate-anilide, m.p. 104-105°) is insoluble. A mixture of these two compounds melts at 54°. The anil does not give any colouration to an alcoholic solution of ferric chloride. It is similar to that described by Kötz and Merkel (*loc. cit.*) who however records a melting point at 29°.

(*ii*) *Formation of* 1: 2: 3: 4-*Tetrahydroacridone.*—The above anil was heated in an oil-bath at 260° for a few minutes when diphenylcarbamide (m.p. 233-235°) sublimed off and condensed in the air condenser and the receiver, while the liquid in the flask was soon transformed into a fine crystalline solid. This was collected, washed with ether and cold alcohol and was finally crystallised from ethyl alcohol. (Found: N, 7·2. $C_{13}H_{13}ON$ requires N, 7·04 per cent.). It melted at 357-358° and was identified as 1: 2: 3: 4-tetrahydroacridone by direct comparison with an authentic specimen prepared by heating anthranilic acid with *cyclo*hexanone according to the method

of Tiedtke (*loc. cit.*), which after two crystallisations from ethyl alcohol melted at 358°. A mixture of this and our compound also melted at the same temperature. The substance is soluble in dilute mineral acids and acetic acid.

Ethyl cyclo***Hexanone-2-carboxylate and*** p-***Toluidine***: *(i) Formation of* ***Ethyl*** 2-p-***Methylanilido-*** Δ^1-cyclo***hexene-1-carboxylate.***—Molecular porportions of the ketonic ester and *p*-toluidine were mixed together and left overnight. Next day the mixture was found to be turbid owing to the separation of water. The flask was then left in a vacuum over fused calcium chloride. But even after a month it was not possible to isolate any solid product from the reaction mixture.

(ii) Formation of 7-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacridone.*—The above dark liquid was heated in an oil-bath, the temperature of which was slowly raised to 265° and kept at that temperature for a few minutes when the di-*p*-tolylcarbamide (m.p. 260°) sublimed off. The residual solid found in the flask was collected, washed with ether and crystallised from alcohol. After recrystallising from the same solvent it melted at 340°. It was also soluble in dilute acids. (Found: N, 6·68. $C_{14}H_{15}ON$ requires N, 6·57 per cent.).

Ethyl cyclo***Hexanone-2-carboxylate and*** m-***Xylidine*** (asymmetric): ***Formation of*** 7 : 9-***Dimethyl*-1 : 2 : 3 : 4-*Tetrahydroacridone.***—A mixture of the ester (4·5 g.) and the xylidine (3·2 g.) was left in *vacuo* over fused calcium chloride. In this case also neither any crystal separated out nor any solid product was isolated. The red solution obtained, after the reaction was complete, was heated in an oil-bath at 260-265°for about 15 minutes when a liquid of *cyclo*ketonic smell and a crystalline solid were collected in the receiver. The crystals thus distilled off, were collected and washed with ether when it melted at 261-263°, which was not depressed by admixture with pure di-*m*-xylylcarbamide.

The contents in the flask set to a crystalline solid which was washed with ether and collected (yield, 4 g.). The substance crystallises from ethyl alcohol in small crystals melting at 316—318°. As usual it was also soluble in dilute mineral acids.

Ethyl cyclo***Hexanone-2-carboxylate*** *and* p-***Aminoacetanilide***: ***Formation of Ethyl*** 2-p-***Acetamino-anilido-*** Δ^1-cyclo***hexene-1-carboxylate*** (***Formula*** VI).—The β-ketonic ester (2 g.) and the amine (1·8 g.) were dissolved in 10 c.c. glacial acetic acid and the solution

was warmed on a water-bath at 60° for 6 hours and then left overnight at the room temperature. Next morning the crystals (1·8 g.) separated were filtered, washed with dilute acetic acid, with cold dilute alcohol and finally with petroleum ether. (Found: N, 9·4. $C_{17}H_{23}O_3N_2$ requires N, 9·27 per cent.).

This anil crystallises from ethyl alcohol in small glistening flakes with a light yellow tinge. It melts at 191·5° ; its alcoholic solution does not impart any colouration to ferric chloride. The substance decomposes on heating; so it was not possible to convert it into a tetrahydroacridone derivative by this method. Next it was heated on a steam-bath with concentrated sulphuric acid for over half an hour. No solid product of any definite constitution was isolated after the subsequent treatment of the reacted mixture, whereas the acid solution was found to contain the mother ester and a primary amine salt as it readily underwent diazotization.

*Action of Ammonia on 2-Hydroxymethylene*cyclo*hexanone.*—Freshly distilled hydroxymethylene*cyclo*hexanone was shaken with a considerable volume of liquor ammonia in a stoppered bottle and the reaction mixture was left overnight. Next morning a moderate quantity of a yellow solid product separatad. The substance crystallised from a mixture of chloroform and petroleum ether and melted at 112°. (Found: N, 11·52. $C_7H_{11}ON$ requires N, 11·2 per cent.).

It is soluble in most organic solvents and in dilute acids, and it gives no sharp colouration with alcoholic ferric chloride. When it is boiled with alkali, ammonia escapes and a red liquid is obtained which smells like hydroxymethylene*cyclo*hexanone and also gives the characteristic colour reaction with ferric chloride in alcoholic solution.

Action of Hydroxylamine on the Amide.—An alcoholic solution of the compound was treated with sufficient hydroxylamine hydrochloride in presence of *excess* caustic soda solution, and the mixture was warmed for about 2 or 3 hours on a water-bath at 50-60° and then left over night. Next day the solution was shaken with ether. The ethereal solution was allowed to evaporate after drying, when the compound began to separate in beautiful long needles. On crystallisation from alcohol it melted at 118°. It is supposed to be the oxime of 2-cyano-*cyclo*hexanone whose melting point as recorded by Auwers, Bahr and Fresse (*loc. cit.*) is 117-118°. It is most likely that the excess of alkali hydrolyses the amide to the original hydroxymethyleneketone

which then reacts with hydroxylamine and gives rise to the cyanoketone in the usual way.

Condensation with Cyanoacetamide.—An intimate mixture of cyanoacetamide (1 mol.) and the above compound (1 mol.) was heated together in an oil-bath for about 10-15 minutes at 130-140° when ammonia was given off and the contents in the flask set to a crystalline mass. This was collected, washed with ether and alcohol and then crystallised from glacial acetic acid with a few drops of water. Prismatic needles, m.p. 301°-302°. (Found: N, 14·92, 15·05. $C_{10}H_{12}O_2N$ requires N, 14·58 per cent.).

The product is sparingly soluble in boiling water and alcohol. It readily dissolves in alkali to a colourless solution from which it is precipitated unchanged by acidulation. It also dissolves in concentrated hydrochloric or sulphuric acid and is precipitated on dilution with water. The constitution of the product was ascertained by comparing it with the quinoline derivative synthesised from hydroxymethylene*cyclo*hexanone and cyanoacetamide by one of us (*loc. cit.*) who recorded that it does not melt even at 290°. A mixture of this and our present compound melted at 302°.

The compound was also hydrolysed with sulphuric acid (80 per cent.) when an acid melting at 266° was isolated by diluting the sulphuric acid solution. An acid m. p. (266-67°) was also obtained from Sen-gupta's quinoline derivative, and the mixture of the two melted at the same temperature.

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Received December 23, 1929.

Action of Light on Silver Bromide.

By A. C. Chatterji and P. S. Macmahon.

It is well known that in the photochemical darkening of silver chloride, small quantities of oxygen are absorbed by the darkened product (see Macmahon, *J. Proc. Asiatic Soc. Bengal*, 1915, **11**, 179). It is unnecessary to quote here the voluminous literature on the subject or to discuss the various theories which have been put forward to account for the nature and composition of the reduction product. Suffice to say that the theory of the formation of a sub-chloride Ag_2Cl, has now been generally discarded; that the existence of an oxychloride, Ag_2OCl, is extremely unlikely; and that the most probable assumption is the formation of a solid solution of dispersed silver particles in the unchanged silver chloride together with varying quantities of free metallic silver depending in amount upon the time and intensity of the exposure to light. The latter theory was put forward in the paper mentioned above by one of us (P. S. M.).

It is now of interest to see whether similar results are obtained by exposure of silver bromide to strong sunlight. For this purpose pure dry silver bromide was sealed up in a special vessel containing pure dry oxygen in a thermostat and the temperature and pressure noted. It was then exposed to sunlight for lengthy periods and any alteration in the volume of oxygen was measured. The bromine given off was absrobed by pure precipitated gold, thus avoiding the danger of the absorbent (Baker, for example used copper for this purpose) being accountable for any absorption of oxygen absorbed.

In all cases absorption of oxygen was clearly apparent and the reduced product was found to contain oxygen.

Silver bromide (prepared from chemically pure silver, dissolved in pure dilute nitric acid, precipitated with pure potassium bromide, washed thoroughly and dried over phosphorus pentoxide for several days in a dark room) was placed in a vessel which was sealed to a bulb containing pure precipitated gold. The bulb was joined to another vessel of the shape of a manometer through a three-way tube, one end of which was drawn to a point and left open for filling the

apparatus with oxygen after exhausting the air already present in it. The other two ends of the tube were joined to the bulb with gold and the manometric vessel respectively. The side of the manometric vessel nearer to the bulb was of a wider diameter than the other limb so as to allow more oxygen to remain in the apparatus when finally sealed. The narrow end of the manometric vessel was drawn to a point and sealed.

The whole apparatus, which was of a size convenient for immersion in a thermostat, was exhausted and filled with pure dry oxygen, allowed to remain in the thermostat for an hour, and then the open end of the three-way tube was sealed off under atmospheric pressure.

On exposure to sunlight, in the course of lengthy periods, by repeated shaking and exposure of fresh surfaces to the sun, an appreciable amount of decomposition was obtained. As in the case of silver chloride, this only amounted to a small portion of the mass of silver chloride in the vessel, inasmuch as the darkened outer layers form a thin protective covering over the bulk of each granule.

The apparatus was again put in the thermostat when sufficient decomposition had taken place, and the sealed end of the manometric vessel was cut open with the entire apparatus under water so that it could be sucked in case an absorption of oxygen had taken place.

The following give the results of typical experiments:—

TABLE I.

In this experiment the absorbent used was not a precipitate of pure gold but gold leaves.

Date when sealed	23. 12. 1921.
Date when opened	6. 1. 1926.
Weight of AgBr exposed	69·2 g.
Volume of O_2 absorbed, reduced to N. T. P.	2·087 c.c.

The above absorption was observed with pure dry oxygen in the tube. The bulb was again sealed with the above exposed AgBr, but instead of dry oxygen, this time was filled with moist oxygen. Absorption of a fresh quantity of oxygen took place.

TABLE II.

Date when sealed	20. 1. 1926.
Date when opened	18. 2. 1926.
Volume of O_2 further absorbed, reduced to N. T. P. ...	0·626 c.c.

Instead of using gold leaves as an absorbent for bromine, in the following experiment pure precipitate of gold was used with a fresh quantity of silver bromide.

TABLE III.

Date when sealed	8. 4. 1926.
Date when opened	20. 1. 1927.
Weight of AgBr exposed	49·9 g.
Volume of O_2 absorbed, reduced to N. T. P.	1·064 c.c.

From the above experiments it has been definitely proved that silver bromide absorbs oxygen in approximately the same amount as that observed in the case of silver chloride. Moreover, the amount of absorption bears no quantitative relation to the mass of silver halide but depends on the extent of surface exposed. The oxygen absorbed was present in the darkened product as could be easily indicated by the production of an alkaline reaction when the reduced product was treated with pure neutral potassium chloride in a platinum or silica vessel. The photochemical darkening of silver bromide was also accelerated by the presence of oxidising agents; pure silver bromide was exposed to diffused day-light in two portions, one under boiled conductivity water, and the other under hydrogen peroxide (10 vol.). The latter changed colour rapidly, while the former only very slowly.

The question remains how to account for the small quantity of oxygen which is always present in the photo-halide. Baker has suggested the formation of an oxychloride in the case of silver chloride. It has been pointed out in the previous paper by one of us (*loc. cit.*) that all the reactions observed by Baker can be explained on the assumption that silver oxide (Ag_2O) is present. Moreover, the similarity in the behaviour of silver chloride and silver bromide in sunlight as regards absorption of small quantities of oxygen by the darkened surface layers can only point to one conclusion, namely, that it must be ascribed directly to the silver itself produced in the photochemical decomposition of the halide. In other words disperse silver in solid solution in the photo-halide is capable of taking up oxygen under the conditions created in the above experiments. This behaviour is analogous to that of colloidal silver which even when prepared by Bredig's method from pure metallic silver, is found to contain oxide necessary

for its stable existence. It has been recently proved (Chapman, Ramsbottom and Trotman, *Proc. Roy. Soc.*, 1925, A, **107**, 100) that when silver is heated in oxygen at a pressure exceeding 0·005 mm. of mercury, it becomes almost completely covered with a film of oxide. Therefore, there is nothing improbable in the assumption that an exothermic reaction of the above type should take place spontaneously under the influence of light, especially when the metal is in such a fine state of subdivision.

Our next step was to endeavour to prepare disperse silver in weighable quantities and to find out if it can be directly oxidised by exposure to oxygen. A method for preparing this material was published by Fürth (*Kolloid Z.*, 1924, **34**, 222), who obtained a deposit from an electric arc struck in air between two silver electrodes, and this powder gave a sol when dissolved in water. We have obtained disperse silver by Fürth's method and have observed that this deposit is by no means pure silver: it contains large quantities of the oxide and the nitrate. On igniting the deposit, brown fumes are given out in perceptible quantities.

The dust has been prepared by us by striking the arc between chemically pure silver electrodes in either air, oxygen or nitrogen. Nitrate was found to be produced in oxygen containing as little as 0·2 per cent. nitrogen. The same result was obtained in nitrogen containing traces of oxygen.

The properties of the solid powder were also investigated. There was evidence that this powder took up a further small quantity of oxygen indicating at least a partial oxidation of finally disperse silver.

The silver rods for the arc were made from pure silver prepared by the reduction of silver chloride with glucose.

A little of the silver dust prepared in air was taken in a crucible and heated gently so as to change the original grey colour into silvery white, and the loss in weight determined.

TABLE IV.

Weight of the freshly prepared dust taken for heating ...	0·2947 g.
Weight of pure silver left after heating	0·2923 g.
Weight of nitrogen and oxygen driven off	0·0023 g.
Amount of nitrogen and oxygen	0·78 per cent.

A little of the same original silver dust was taken and exposed in a desiccator in an atmosphere of dry oxygen free from carbon dioxide in sunlight to find if it absorbed a further quantity of oxygen during exposure.

TABLE V.

Weight of the original Ag dust taken for further exposure ...	0·2226 g.
Weight of the dust after a week's exposure	0·2235 g.
Weight of the pure silver left after heating	0·2209 g.
Percentage of O_2 and N_2 to pure silver left	1·18 per cent.

From the above table it is seen that there is absorption of a further small quantity of oxygen during exposure.

Another sample of the disperse silver was again prepared by striking the arc in air and was divided into two equal parts, one was directly exposed to dry oxygen in sunlight and was then analysed; the other sample was weighed first and then exposed to dry oxygen in sunlight. The results obtained showed again that there was an increase in weight during exposure. Both these samples contained 0·8489 g. of nitrogen and oxygen for every 100 g. of pure silver produced on heating. In both the cases, the total quantity of nitrogen and oxygen after final exposure was found to be the same.

TABLE VI.

Weight of exposed dust taken	0·1316 g.
Weight of pure silver left on heating	0·1296 g.
Weight of nitrogen and oxygen	0·0020 g.

TABLE VII.

Weight of dust taken for exposure	0·1307 g.
Increase of weight due to the exposure	0·0009 g.
Weight of pure silver left after heating	0·1296 g.
Weight of N_2 and O_2 before exposure	0·0011 g.
Weight of N_2 and O_2 after exposure	0·0020 g.

From the above tables it is clear that finely divided silver is capable of further oxidation. It is of interest to note that the amount of volatile matter in the different samples of silver dust prepared by striking the arc in air, differs by a small quantity. In one case it was 0·7863 g. and in the other, it increased to 0·8489 g. per 100 g. of silver produced on heating the dust. It is evident that the amount of nitrogen and oxygen in the dust will necessarily depend on the size of the particles, and it is just possible that the size of the silver grains is not uniform even when the experiments are repeated under apparently identical conditions.

At present there seems to be enough experimental evidence in support of the view advanced in a former paper (*loc. cit.*) by one of us that molecular or colloidal silver is capable of being spontaneously oxidised in air. This being firmly established we venture to suggest that the formation of a photo-halide is due partly at least to the direct absorption of oxygen by the disperse silver produced in photochemical decomposition of the silver halide and is not due to the photochemical synthesis of an oxy-compound.

Summary.

1. Pure dry silver bromide was sealed in a tube with oxygen using gold as an absorbent, and was then exposed to the tropical sun for lengthy periods. Absorption of oxygen occurred in all cases almost to the same extent as in the case of silver chloride.

2. The amount of absorption bears no quantitative relation to the mass of the silver halide exposed, but depends on the extent of surface exposed.

3. Oxygen is present in the darkened product.

4. The photochemical darkening of silver bromide is accelerated by the presence of oxidising agents.

5. Disperse silver was produced by striking an arc between two pure silver electrodes in air, oxygen and nitrogen. It has been found that the dust so prepared is by no means pure silver but is contaminated with oxide and nitrate in varying quantities.

6. Disperse silver produced in air is capable of further oxidation though to a small extent when exposed to dry oxygen.

7. The photo-halides formed are not due to the photochemical synthesis of an oxy-compound but are due partly at least to the direct absorption of oxygen by the disperse silver produced in the photochemical decomposition of silver halide so as to produce a partial oxidation of the disperse silver formed.

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P. S.—Our attention has been drawn to a recent paper (Chapman and Hall, *Proc. Roy. Soc.*, 1929, **124**, 478) in which the authors confirm the conclusion arrived at in this paper as regards the spontaneous oxidation of silver. They found that at the same temperature and pressure hydrogen molecules removed less heat from a hot metalic silver surface than from a surface of the same metal which has been subjected to the action of oxygen, indicating the formation of a surface layer of oxide.

They have also found from observations on the catalytic activity of silver wire that even at ordinary temperature a silver surface exposed to oxygen is immediately covered with a film of oxide.

Adsorption of Benzol Vapour by Mixed Adsorbents.

By Jogendra Kumar Chowdhury and Hemendra Nath Pal.

In a previous paper (Chowdhury and Bagchi, *J. Indian Chem. Soc.*, 1928, **5**, 122) it was shown that specially prepared mixed adsorbents had a very high adsorption capacity and this fact was utilized for the desulphurisation of mineral oils. It is now intended to study the properties of the mixed adsorbents further with a view to find a suitable adsorbent for benzol and also to extend the study of mixed adsorbents to bauxite, a mineral, which owing to its physical properties, particularly its hardness, is preferred as an adsorbent in several industries. Artificial adsorbents such as silica gel and activated carbon are liable to crumble to very fine dust on repeated use. Activated carbon though characterised by its high adsorption capacity for benzol hydrocarbons, is pyrophorous in nature, and hence liable to catch fire, specially when heat is evolved in the course of adsorption. This property makes its regeneration by the simple process of roasting in an oxidising atmosphere impossible. It is therefore of great interest to investigate if a substitute could be found in a hard mineral like bauxite, which occurs in India in extensive deposits within easy reach of the larger coke-ovens and can be obtained at a nominal cost.

The determination of adsorption capacity was made by the dynamic method, in preference to the static method, as the former is simpler from experimental point of view and corresponds more closely to the large scale practice. The following arrangement was used for the purpose:

Dry air was passed at a constant rate of 180 c.c. per minute through a double-walled vessel *B*, containing a definite amount of benzol and placed in a thermostat *C*. The benzolised air then passed through a coil surrounding the adsorption vessel *A* (Fig. I), which was placed within a wider tube, entering it at the bottom. The temperature of both the vessels *A* and *B* were kept constant, usually at 26°, by means of the thermostat, the coil serving to bring

the gas to the same temperature before adsorption actually took place. The adsorption tube was attached to the coil by means of ground -glass joint and could be detached and weighed before and after each adsorption. Concentration of benzol vapour in the air could be changed if necessary by regulating the temperature of the thermostat and the rate of flow. If desired, fresh air might also be mixed with the benzolised air, as it came out of the vessel *B*. In each case the vapour was passed until the weight of the adsorbent was practically constant.

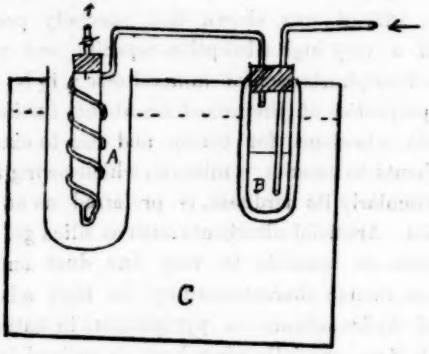


Fig. I.

Adsorption by Artificially Prepared Mixed Adsorbents.

The following mixed adsorbents were prepared and their activities studied with the help of the arrangement described above.

(1) Mixed alumina and activated carbon.
(2) Mixed alumina and silica gels.
(3) Mixed alumina and ferric oxide gels.

Mixed alumina and activated Carbon.—The mixed adsorbent was prepared by precipitating alumina on finely divided activated carbon followed by washing and drying, and finally activated by heating in a current of air to 220−230° in an electric furnace.

The percentage of the components of the mixed adsorbent was varied and their adsorption capacities ascertained. These are noted in the following table and graphically shewn in Fig. II, Curve 1.

TABLE I,

Size of the particles = 30 − 60 mesh. Temperature = 26°.

Concentration of benzol vapour in air = 1·2 per cent. by vol.

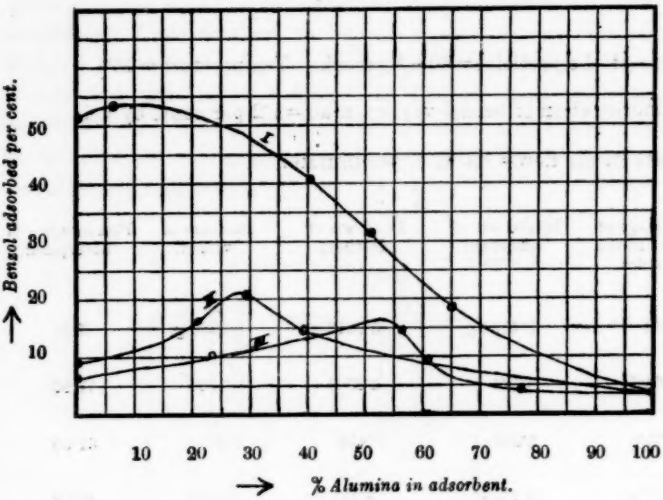
Rate of air flow = 180 c. c. per minute.

Percentage of Al_2O_3 in the mixture.	Initial wt. of adsorbent.	Final wt. of adsorbent.	Increase of weight.	Percentage of adsorption.
100	3·5124 g.	3·6412 g.	0·1288 g.	3·67
64·7	4·124	4·8606	0·7366	17·86
51·8	2·589	3·415	0·826	31·90
41·4	2·2218	3·111	0·8892	40·03
6·73	0·2588	0·3966	6·1378	53·246
0	0·3305	0·4994	0·1689	51·10

It will be observed that alumina gel has a very slight activity (3·67%) as compared to activated carbon (51·1%), and only a slight increase in the adsorption capacity is obtained by the mixture containing 6·73 per cent. of Al_2O_3. Deposition of inorganic gels on activated carbon makes it, however, less inflammable (Berl, D. R.-P. 375658).

(2) *Mixed alumina and silica gels.*—The mixed adsorbent was prepared by suspending aluminium hydroxide in sodium silicate solution and adding hydrochloric acid under constant stirring until the solution was slightly alkaline, stirring being continued until silica gel completely precipitated. The mixed precipitate was then activated by heating to 220−230° in an electirc furnace in a current of dry air. The proportion of the components was varied by taking different amounts of sodium silicate from a stock solution of known strength The results obtained with different pecentages of alumina are shown in the following table (Fig. II, Curve II).

Effect of Composition on Adsorption Capacity.



Fig, II.

I = Adsorption of benzol by mixed alumina and activated carbon.
II = ,, ,, ,, ,, ,, silica gel.
III = ,, ,, ,, ,, ,, ferric oxide gel.

TABLE II.

Experimental conditions same as in Table I.

Percentage of alumina in the adsorbent.	Initial wt. of adsorbent.	Final wt. of adsorbent.	Increase of weight.	Percentage of adsorption.
0	3·556 g.	3·903 g.	0·347 g.	9·76
21·8	0·156	0·1816	0·0256	16·41
27·9	0·521	0·6263	0·1053	20·21
35·2	0·1175	0·1357	0·0182	15·48
38·46	0·1123	0·1282	0·016	14·25
100	3·5124	3·6412	0·1288	3·67

Mixed alumina and ferric oxide gels.—The mixed adsorbent was prepared by taking different amounts of ferric and aluminium sulphates from their stock solutions of known strength in a beaker

and precipitating their hydroxides simultaneously in the usual manner. The mass was carefully washed, dried and activated as in the previous case. The iron content of the mixed adsorbent was determined volumetrically by titration with potassium dichromate. The results of the experiments are shown in the following table and in Curve III, Fig. II. As in previous cases the adsorption reaches a miximum (14·29 per cent.) with definite percentages of Fe_2O_3 in the mixture, while pure alumina gel adsorbs 3·67 per cent. and ferric oxide gel 7·2 per cent. only under the same conditions. The increase in adsorption is, however, smaller than the previous instance.

TABLE III.

Conditions same as in Table I.

Percentage of Al_2O_3 in the mixture.	Initial wt. of adsorbent.	Final wt. of adsorbent.	Increase of weight.	Percentage of adsorption.
0	1·341 g.	1·4376 g.	0·0966 g.	7·2
22·7	0·8618	0·9496	0·0878	10·19
56·9	1·4062	1·6072	0·2010	14·29
61·1	0·8376	0·9152	0·0776	9·26
75·8	0·9492	0·9904	0·0412	4·34
100	3·5124	3·6412	0·1288	3·67

It may be noted that this rise in the activity of mixed adsorbents is observed only when they are formed by simultaneous precipitation or by the formation of one adsorbent in the pores of the other. Mechanical mixtures, however intimately they might be mixed together, show no increased activity.

Bauxite as an Adsorbent for Benzol Vapour.

Having determined the properties of mixed alumina and ferric oxide gels, it is now intended to study the properties of bauxite which is a natural mixed adsorbent composed mainly of alumina and ferric oxide. Bauxite has been used for a long time as an adsorbent in petroleum industry. It has been found that some bauxites are highly active while others are comparatively inert and no satisfactory explanation has so far been put forward to explain this difference. It is well known that the adsorption capacity of bauxite does not depend on its alumina content or on any other component. In the light of the following experiments it will be seen that the adsorption

capacity of bauxite corresponds very closely to that of mixed adsorbents and depends on a suitable proportion of Al_2O_3, Fe_2O_3 and SiO_2 contents. It is likely that one adsorbent is formed in the pores of the others, thus increasing the number of very fine capillary pores which would naturally enhance the activity.

Bauxite used in these experiments gave the following analytical data:—

Al_2O_3	... 69·15 per cent.	SiO_2	... 0·91
Fe_2O_3	... 23·2	TiO_2	... 1·5

The mineral was powdered and heated to 330-350° in a current of dry air for two hours and cooled before its adsorption capacity was determined. The concentration of benzol vapour in the gas was varied and the results obtained are noted in the following table and shown graphically in Fig. III.

Adsorption Isotherm with Bauxite as Adsorbent (26°).

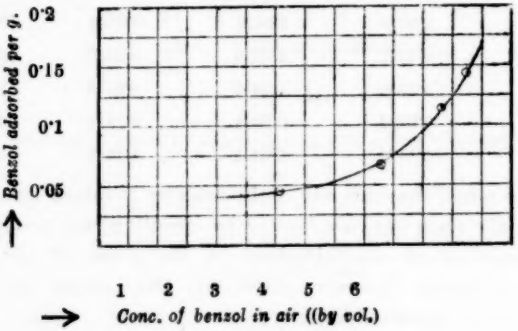


Fig. III.

TABLE IV.

Conditions same as in Table I.

Percentage of benzol in air by vol.	Initial wt. of adsorbent.	Final wt.	Increase of wt.	Percentage of adsorption.	Amount adsorbed per g.
0·79	0·3326 g.	0·3524 g.	0·0198 g.	5·95	0·0595
1·2	1·351	1·4648	0·1138	8·42	0·0842
2·3	0·1848	0·2092	0·0244	13·2	0·132
3·9	0·2026	0·234	0·0314	15·49	0·1549

It will be observed that the adsorption varies with concentration as is to be expected from Freundlich's equation, the curve being of the nature of a parabola.

The adsorption figures for bauxite are considerably higher than those of either alumina gel or ferric oxide gel, but on the whole are lower than those of the mixed alumina and ferric oxide gels prepared in the laboratory. This is however, only to be expected in view of difference in the conditions of formation of the two absorbents. When the concentration of benzol in the air corresponds to that in which it is generally present in coal or coke-oven gas (0·79 per cent. by vol.), the adsorption comes to only 5·95 per cent. which is rather too low a figure for the large scale application of bauxite. The following experiments represent attempts to investigate if bauxite could be activated further with a view to make its industrial application as an adsorbent for benzol possible.

Activation of Bauxite.

(a) *Activation of bauxite by deposition of ferric oxide gel.*—The first idea that suggests itself for the activation of bauxite is to deposit ferric oxide gel on it so as to bring up its iron content to correspond to the amount found most suitable in the mixed alumina and ferric oxide gels. For this purpose finely divided bauxite was suspended in a solution of ferric sulphate, and ferric hydroxide was precipitated in the usual manner under constant stirring. This was washed, dried and activated at 330—350°. The results of adsorption are noted in the following table.

TABLE V.

Conditions same as in Table I.

Percentage composition of adsorbent in the mixture: Fe_2O_3.	Al_2O_3.	Initial wt. of adsorbent.	Final wt.	Increase of wt.	Percentage of adsorption.
51·9	43·1	0·4738 g.	0·5256 g.	0·0518	10·93
47·6	45·6	1·2108	1·3718	0·161	13·3
38·9	53·5	1·3508	0·5102	0·1594	11·8

It will be observed from the above table that as in the case of mixed adsorbent, the activity of bauxite increases with the increase of ferric oxide content until the latter reaches 47·6 per cent. when it adsorbs 13·3 per cent. of benzol; the maximum in the case of mixed

alumina-ferric oxide gels with 43·1 per cent. of ferric oxide (or 56·9 per cent. of alumina) being 14·29 per cent. The following data show that increased activity is not noticed when bauxite and ferric oxide gels are mixed mechanically. It is evident that the ferric oxide must be precipitated within the pores of the bauxite.

TABLE VI.

Adsorption by Mechanical Mixtures of Bauxite and Ferric Oxide.

Conditions same as in Table I.

Percentage composition of adsorbent: Fe_2O_3	Al_2O_3	Initial wt. of adsorbent.	Final wt.	Increase of wt.	Percentage of adsorption.
45·9	47·0	0·4708 g.	0·5074 g.	0·0366 g.	7·77
73·1	21·2	0·917	0·9818	0·0648	7·07

(*b*) *Activation of bauxite by deposition of silica gel.*—Attempts were then made to activate bauxite further by the precipitation of silica gel in place of ferric oxide, the method of preparation and activation being the same as before. The results obtained by the deposition of different quantities of silica gel are shown in the following table and the corresponding curve in Fig. IV.

Adsorption by Silicalised Bauxite.

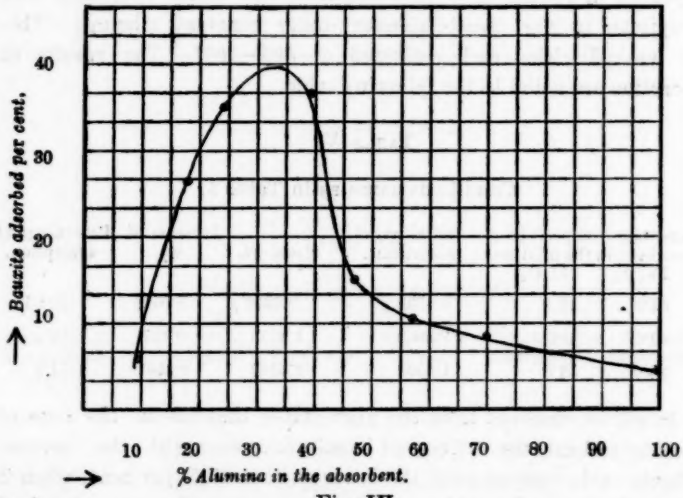


Fig. IV.

TABLE VII.

Conditions same as in Table I.

Percentage composition of adsorbent : SiO_2	Al_2O_3	Fe_2O_3	Initial wt. of adsorbent.	Final wt.	Increase of wt.	Percentage of adsorption.
15·07	57·04	19·5	1·155 g.	1·2712 g.	0·1162 g.	10·06
29·8	47·5	16·2	1·2148	1·4031	0·1883	15·5
40·8	39·7	13·6	1·2086	1·6667	0·4581	37·9 (M_1)
60·1	26·8	9·2	1·1366	1·526	0·3894	34·26(M_2)
76·2	16·7	5·7	1·344	1·72	0·376	27·98(M_3)
82·3	9·9	6·4	0·273	0·2918	0·0188	6·15

A mechanical mixture of silica and bauxite containing 43·04 per cent. of SiO_2, 38 3 per cent. of Al_2O_3, 13·28 per cent. of Fe_2O_3 was also tried under the same conditions. Its adsorption capacity was found to be only 6·65 per cent.

It is satisfactory to note from the above table that an enormous increase in adsorption capacity of bauxite may be effected by the deposition of silica, thus while bauxite and silica gel adsorb 8·42 per cent. and 9·76 per cent. respectively, the silicalised bauxite with 40·8 per cent. of SiO_2 adsorbs 37·9 per cent. The adsorption capacity of such activated bauxite for benzol at low concentration is much higher than any other inorganic adsorbent and compares favourably with activated carbon without having the defects of the latter mentioned previously. It is, however, necessary to test if this adsorbent will stand the drastic conditions prevailing in gas works and coke-ovens.

Possibility of using Silicalised Bauxite for the Recovery of Benzol from Coal Gas.

A suitable adsorbent for this purpose should naturally remain unaffected both chemically and physically when it comes in contact with coal or coke-oven gases under drastic conditions prevailing in the works and should be capable of regeneration to practically its original activity. It is now intended to study if sulphuretted hydrogen and other constituents of coal gas will have any unfavourable effect on the adsorbents and if the adsorbent exposed to tarry matter may be revivified. For the purpose of these experiments, the mixed adsorbent, M_3 was used, as this mixture happened to be in stock in large amount.

Effect of Sulphuretted Hydrogen.

It was found that dry sulphuretted hydrogen when passed through the adsorbents at 26° in the usual manner was immediately oxidised and sulphur was deposited on the adsorbent, the increase in the weight of the adsorbent being 5·1 per cent. By washing the absorbent with carbon disulphide 3·8 per cent. of free sulphur could be recovered. It will thus be observed that the adsorbent helps to purify coal gas with the recovery of free sulphur at ordinary temperature. The adsorbent was tested for sulphide and sulphate but no trace of either could be detected. The adsorbent was evidently chemically inert to the action of sulphuretted hydrogen.

In order to determine the amount of adsorbed benzol, a mixture of air, benzol, and H_2S was passed through the adsorbent until the increase in weight was practically constant. The mixture was obtained by taking H_2S from a burette at a definite rate and mixing it with air by means of a T-tube just before the latter entered the vessel containing benzol. The concentrations of benzol and H_2S were respectively 1·2 per cent. and 0·51 per cent. by volume, the actual concentration of H_2S in crude coal gas being 0·4—1·6 per cent. by volume (Rogers, "Industrial Chemistry," p. 497).

The increase in weight of the adsorbent was 24·15 per cent. as compared to 27·98 per cent. for the benzol vapour alone. It appeared that though H_2S was completely oxidised (as no smell of H_2S could be detected after adsorption), it did not materially affect the adsorption of benzol. The results of adsorption are given in Table IX.

As the adsorbent is not chemically acted upon, it may be expected that the adsorbent exposed to the action of H_2S will be capable of regeneration to almost its original strength and this has been found to be actually the case as will be evident from the following table.

TABLE VIII.

Time of roasting = 2 hrs.; other conditions same as in Table I.

Treatment of adsorbent.	Temp. of regeneration.	Initial wt.	Final wt.	Increase of wt.	Percentage of adsorption.
Roasted.	330-350°	0·698 g.	0·874 g.	0·176 g.	25·21
Washed with CS_2 and then roasted.	400°	0·502	0·6331	0·1311	26·12
,, ,,	490-510°	0·41	0·5236	0·1136	27·7

The Effect of Carbon Monoxide.—Carbon monoxide passed through the adsorbent M_3, from a burette at the constant rate of 2 c.c. per minute increased the weight of the adsorbent by 1·22 per cent. only. Mixed with air and benzene vapour it was passed again through the adsorbent, the concentrations of carbon monoxide and benzol vapour being 4·4 per cent. and 1·2 per cent. by volume respectively. The increase in the weight of the adsorbent was 27·99 per cent. from which it is evident that carbon monoxide did not exercise any adverse effect on the adsorption of benzol. The results are given in Table IX.

The Effect of Ethylene.—It has been maintained by different investigators that unsaturated hydrocarbons polymerise within the pores of the adsorbent (Dunston and others, *J. Soc. Chem. Ind.*, 1924, **43**, 179T) forming sometimes tarry matter and thereby affecting the adsorption capacity. Ethylene vapour, however, did not affect the adsorbent in any such manner. Ethylene gas was collected in a large vessel over water and was passed through the adsorbent in the usual manner, the increase in weight of the adsorbent being only 1·32 per cent. Mixed with equal volume of air, ethylene was passed again through the adsorbent which increased in weight by only 0·33 per cent. The adsorbent thus exposed to the action of ethylene vapour, was heated in a current of air and the regenerated mass adsorbed 27·2 per cent. benzol. Ethylene vapour did not evidently cause any material injury to the adsorbent. The results are given in the following table.

TABLE IX.

Conditions same as in Table I.

Composition of gases.	Rate of gas flow per min.	Initial wt.	Final wt.	Increase of wt.	Percentage of adsorption.
1. Dry H_2S ...	180 c.c.	1·0488 g.	1·1023 g.	0·0535 g.	5·1
2. Dry H_2S (0·51%) benzene (1·2%) and air ...	180	0·414	0·514	0·1	24·15
3. Carbon monoxide	2	0·384	0·3887	0·0047	1·22
4. CO (4·4 %) C_6H_6 (1·2%) and air ...	180	0·318	0·407	0·089	27·99
5. Ethylene ...	180	0·908	0·92	0·012	1·32
6. Ethylene and air (equal vol.) ...	,,	0·2458	0·2466	0·0008	0·33

The Effect of Water Vapour.—It is important to note the effect of water vapour on the adsorbent, as the pores of many adsorbents are easily moistened by water vapour and thereby the adsorption of hydrocarbons may be prevented. Large quantities of water vapour may even wash off any benzol already adsorbed.

Air containing 3·02 per cent. water vapour by volume was passed through the adsorbent which increased by 21·6 per cent. by weight. It was therefore necessary to determine which of the two constituents, water vapour or benzol vapour was selectively adsorbed.

A mixture of water vapour (3·02 per cent. by vol.), benzol (1·2 per cent by vol.) and air was passed through the adsorbent which increased 25·82 per cent. by weight. In order to determine the proportion of water and benzol in the adsorbed mass, it was then heated in a horizontal glass tube while a dry current of air was passed through. The water vapour in the escaping gas was absorbed by means of calcium chloride tubes. The increase in weight was due to 4·8 per cent. of water and 21·02 per cent. of benzol.

It will be seen that water vāpour itself does not lower the absorption to a very great extent though it must be remembered (Williams, *J. Soc. Chem. Ind.*, 1924, **43**, 97T.) that long continued passage of the gas containing water vapour may ultimately wash off the absorbed benzol. It is necessary to stop the passage of the gas mixture at a suitable moment after an hour or two when the proportion of benzol in the adsorbent is the greatest.

Effect of tarry Matter on Regeneration of the Adsorbent.—The adsorbent M_3 was soaked with a little tar subjected to roasting in a current of dry air. The absorption capacity of the regenerated mass is shown in the following table.

TABLE X.

Conditions same as Table I.

Temp. of roasting.	Initial wt. of adsorbent.	Final wt. of adsorbent.	Increase of wt.	Percentage of adsorption.
300-310°	0·2378 g.	0·2672 g.	0·0294 g.	12·36
420-430°	0·1258	0·1523	0·0265	21·07
540-560°	0·541	0·6877	0·1467	27·12

It will be observed that it is necessary to heat the adsorbent to higher temperature (540-560°) to recover its original activity, as the carbonaceous matter in the pores must be completely burnt off,

The unchanged activity of the adsorbent indicates that it is not changed by subjecting it to the above temperature.

Effect of Temperature on Absorption.—In order to determine the efficiency of the absorbent M_2, under different climatic conditions, its activity was determined at three different temperatures, 19°, 26° and 35°. The efficiencies of absorption are noted below.

TABLE XI.

Conditions (excepting temp. of the thermostat) same as in Table I.

Temp.	Initial wt.	Final wt.	Increase of wt.	Percentage of adsorption.
19°	0·21 g.	0·2884 g.	0·0784 g.	37·33
26°	0·32	0·4293	0·1093	34·16
35°	0·1101	0·1355	0·0254	23·07

Discussion.

It will be observed from the above experiments that silicalised bauxite is eminently suitable for the adsorption of benzol vapour. The above figures have been obtained with the adsorbent M_3, but much higher figures would be obtained by using the adsorbent M_1, which adsorbs 37·9 per cent. of benzol in comparison with 27·98 per cent. by M_3. The advantages of using this adsorbent in preference to others, have already been indicated. The following considerations will show that it is also preferable to adsorption by wash-oil which is generally used.

It is well known that the benzol obtained by wash-oil process is highly coloured and is mixed with "prebenzol" as well as with lighter fractions of creosote which is used as wash-oil. The wash-oil benzol has therefore to be subjected to long continued fractionation before it can be used even as motor-spirit. It has been shown by Williams (*loc. cit.*) that the benzol obtained by the adsorption process is good in colour and requires little or no fractionation. It further requires no washing with sulphuric acid (as in the case of wash-oil benzol) which naturally destroys a considerable fraction of the benzol. The yield of benzol by the adsorption process is therefore quite satisfactory.

It may also be noted that the adsorbent or the wash-oil as the case may be, has to be heated to at least 120-140° to drive

off the crude benzol (containing toluene and xylene) and subsequently cooled to ordinary temperature. As alumina has a very low specific heat, the quantity of heat used in the above process should therefore be small in comparison with that required for wash-oil process.

It may further be observed that silicalised bauxite adsorbs 37·9 per cent. while wash-oil only 3—4 per cent. of benzol. To recover the same quantity of benzol, a large quantity of wash-oil has therefore to be heated in comparison with silicalised bauxite. The use of the adsorption process should therefore cause a saving in the cost of fuel. Further, as the benzol may be obtained in fairly good quality and may be used direct for motor-spirit, the cost of rectification even for pure benzol would be considerably less than that in the wash-oil process.

Summary.

(1) It has been observed that the mixed adsorbents formed by simultaneous precipitation of two or more adsorbents or by precipitation of one adsorbent within the pores of the other have very high adsorption capacity for benzol vapour. The amount of increase in adsorption depends on suitable proportion of different ingredients of the mixed adsorbents and on the nature of those ingredients.

(2) The enhanced activity of bauxite as an adsorbent has been explained by the fact of its being a natural mixed adsorbent.

(3) The adsorption capacity of bauxite for benzol vapour has been enormously increased (from 8·42 to 37·9 per cent.) by deposition of silica gel.

(4) This silicalised bauxite has been tested under different conditions similar to those prevailing in gas-works and coke-ovens and has been found suitable. It is not changed either chemically or physically under the action of different ingredients of coal gas and may be regenerated by the simple process of roasting in the air, to almost its original activity.

(5) The advantages of the use of silicalised bauxite in place of wash-oil is shortly discussed.

In conclusion, we beg to offer our best thanks to the Director of Geological Survey, Calcutta, for placing some samples of Indian bauxite at our disposal for the purpose of these investigations.

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Received October 24, 1929.

On the Effect of Dilution on the Coagulation of Arsenious Sulphide Hydrosols in its Relation to the Arsenious Oxide Content.

By Jnanendra Nath Mukherjee and Santosh Chandra Ganguly.

Recent measurements (Mukherjee and co-workers, *J. Indian Chem. Soc.*, 1928, **5**, 627, 733)* of the cataphoretic speeds of particles of colloidal arsenious sulphide under different conditions show (*a*) that the speed decreases on dilution as also on the addition of arsenious oxide* and (*b*) that these two factors show some similarities regarding the manner in which the speeds change when different concentrations of potassium chloride are added to the sol, but (*c*) there is no parallelism between the initial cataphoretic speeds (when no electrolyte has been added) and those at precipitating concentrations of the electrolyte.

Dhar (*J. Phys. Chem.*, 1927, **31**, 349, reference to earlier papers are given therein) has classified colloids as normal and abnormal depending upon their behaviour on dilution. He assumes that the precipitation takes place at the isoelectric point and emphasises that "normally" a colloid requires on dilution a smaller precipitating concentration of an electrolyte. Where the reverse happens, he considers that the relative adsorption of similarly charged ions increases and is responsible for the higher precipitating concentration. In the case of arsenious sulphide, Dhar (*Kolloid Z.*, 1925, **36**, 129) has also discussed the effect of dilution in terms of the variation of the contents of arsenious oxide and hydrogen sulphide. In view of the above observations regarding the cataphoretic speeds the behaviour on dilution of this sol containing different amounts of arsenious oxide, has been studied.

Results and Discussion.

The method of determining the coagulating concentrations was as given in earlier papers from this laboratory. 5 C.c. of the sol

* Also results obtained by S. N. Mukherjee shortly to be published.

were always mixed with an equal volume of the electrolyte. Sol A was prepared with a restricted amount of hydrogen sulphide. A saturated solution of arsenious oxide was diluted with twice its volume of water. Equal volumes of the resulting solution and of a solution of hydrogen sulphide were mixed such that part of the oxide was left unconverted into the sulphide. It contained 0·0105 g.-moles of the sulphide and 0·0315 of the oxide per litre. Sols B and C which were mixed with just enough hydrogen sulphide and were free from the oxide had 0·042 and 0·039 gram-moles of the sulphide respectively. A brisk stream of hydrogen was passed to ensure that there were no excess of the sulphide or oxide. The dilutions are given as the ratio of the volume of the stock sol to the volume of water added to it before mixing with the electrolyte. The results with sols A and B are given below.

TABLE I.

Dilution.	$BaCl_2$		HCl		KCl		LiCl	
	Sol A	Sol B	Sol A	Sol B	Sol A	Sol B	Sol A	Sol B
1 : 0	0·0014	0·00135	0·037	0·052	0·055	0·071	0·064	0·084
1 : 1	0·0017	0·00145	0·042	0·058	0·070	0·082	0·081	0·101
2 : 3	0·0020	0·0015	0·045	0·061	0·074	—	0·092	0·106
1 : 4	0·0022	0·0018	—	0·066	0·075	0·102	—	0·132

Usher (*Trans. Faraday Soc.*, 1926, **21**, 406) advocates the comparison of the coagulating concentrations of the different dilutions which would produce the same effect in intervals proportional to dilution. As the rate of coalescence depends upon the number of particles in unit volume (*i.e.*, on the dilution) the same stage of coalescence will be reached at different times and therefore the above procedure was perhaps intended to show separately the influence of factors other than the decrease in the number of particles per unit volume. It would appear (Smoluchowski, *Z. physikal. Chem.*, 1917, **92**, 129) that this procedure does not wholly obviate the difficulty as the different stages of coalescence are not strictly comparable. The results with sol C following this procedure are however given in the following table.

TABLE II.

Dilution : Sol C	$BaCl_2$		HCl		KCl		LiCl	
	Conc. in *N*.	Time in min.	Conc. in *N*.	Time in min.	Conc. in *N*.	Time in min.	Conc. in *N*.	Time in min.
1 : 0	0·00125	3	0·043	3	0·059	3	0·066	3
1 : 2	0·00125	6	0·046	6	0·066	6	0·080	6
2 : 3	0·00122	9-10	0·048	9-10	0·070	9-10	0·080	9-10

In the above tables one notices a uniform stabilisation on dilution for all the electrolytes excepting barium chloride in Table II. The observations with barium chloride are contrary to the experience of previous workers but agree with those of Mukherjee and Sen (*J. Chem. Soc.*, 1919, **115**, 461). Usher's procedure also shows a stabilising effect of dilution excepting the first column (Table II).

Two sols having the same sulphide content but prepared as below were next compared. Sol E was prepared by dilution from sol D which had a higher sulphide content namely, 0·036 gram-moles per litre. Sol F was prepared in the usual way.

TABLE III.

Sol	HCl	KCl	LiCl	$BaCl_2$
D	0·043	0·059	0·068	0·0013
D/2	0·048	0·069	0·085	—
E	0·045	0·062	0·074	0·00135
E/2	0·053	0·074	0·096	—
F	0·046	0·063	0·074	0·00135
F/2	0·050	0·075	0·093	—

Here also dilution results in stabilisation. The coagulating concentrations for sols E and F are very nearly the same. It appears therefore that with a constant procedure for preparation the behaviour depends to a large extent on the sulphide content.

The influence of arsenious oxide has been studied from two different standpoints. In one series, G, different percentages of arsenious oxide were left unconverted by regulating the quantity of saturated hydrogen sulphide but the total arsenic content was kept the same. In the second series, H, quantities of saturated solution

of arsenious oxide and water were added from outside to a stock sol so as to bring their total arsenic content and the relative amo' nts of arsenious oxide and arsenious sulphide to exactly the same values as those of the corresponding sol G.

Series G/2 and H/2 were prepared by diluting the corresponding sols with an equal volume of water. The number of atoms of arsenic in the form of the free oxide has been given in round figures as percentages of the total number of atoms of arsenic in a definite volume. The total arsenic content in series G and H were 0·042 gram-atoms of arsenic per litre.

TABLE IV.

Series G and G/2.

Percent. of		$BaCl_2$		HCl		KCl		LiCl	
Oxide	Sulphide	G	G/2	G	G/2	G	G/2	G	G/2
0	100	0·00135	0·0014	0·056	0·063	0·068	0·079	0·080	0·094
5	95	0·00135	0·0014	0·034	0·037	0·043	0·051	0·048	0·060
15	85	0·00135	0·0015	0·032	0·036	0·041	0·051	0 050	0·052
35	65	0·00135	0·0015	0·031	0·036	0·043	0·053	0·050	0·062
55	45	0·00135	0·0016	0·032	0·036	0·044	0·056	0·052	0·060
80	20	0·00145	0·0018	0·034	0·037	0·048	0·065	0·058	0·072

TABLE V.

Series H and H/2

Percent. of		$BaCl_2$		HCl		KCl		LiCl	
Oxide	Sulphide	H	H-2	H	H-2	H	H-2	H	H-2
0	100	0·00135	0·0014	0·056	0·063	0·068	0·079	0·080	0·094
5	95	0·00130	0·00145	0·036	0·041	0·048	0·058	0·057	0·069
15	85	0·00130	0·00150	0·036	0·042	0·050	0·060	0·057	0·073
35	65	0·00135	0·00155	0·037	0·044	0·051	0·063	0·062	0·076
45	55	0·00140	0·00160	0·037	0·044	0·053	0·068	0·062	0·076

Series G and H show on the whole a similar behaviour. There is a marked lowering of the coagulating concentration so far as the univalent cations are concerned when the percentage of sulphide

changes from 100 to 95. On further decrease of the sulphide content the coagulating concentrations change only slightly but at the lowest percentages of the sulphide they show a perceptible increase. Thus the sensitisation is followed by stabilisation. The coagulating concentrations of barium chloride show a similar behaviour with the difference that sensitisation is not observed. Further the observed stabilisation with univalent cations is not so marked as the sensitisation but with barium chloride the stabilisation is quite marked. Comparing the corresponding members of G and G/2 or H and H/2 series it will be observed that dilution invariably results in stabilisation but the percentage change in the coagulating concentration fairly remains constant, independent of the ratio of sulphide to oxide. The coagulating concentration of barium chloride increases with dilution in all these cases. It would seem that these sols in which there was little or no free hydrogen sulphide in excess (and in most cases there was an actual excess of free arsenious oxide) show a characteristic behaviour in this respect.

The first horizontal rows in Tables IV and V give the coagulating concentrations of the same sol. A comparison of the corresponding members of series G and H will show that the coagulating concentration for series H are in general higher than that for series G with the exception of barium chloride which gives practically the same concentration for both series and in some cases gives a smaller concentration for series H. The two series are not identical and even with these slight differences in the method of preparation the properties of the sol are not determined by the sulphide and oxide content.

The stabilisation with decreasing sulphide content and increasing oxide content observed with barium chloride, requires more detailed discussion. It has been taken for granted by previous workers (Dhar, *loc. cit.* ; see however, Mukherjee and Sen, *loc. cit.*) that dilution of this colloid has always a sensitising action against coagulation by barium chloride. In the case of monovalent cations dilution has always been observed, on the contrary, to produce a stabilising action. Reference has been made before to the fact that on increasing the amounts of arsenious oxide while keeping the sulphide content constant, it is observed that the coagulating concentrations of both potassium and barium chloride diminish. It has also been stated that the cataphoretic speed shows a regular decrease under the same conditions. The observed sensitising action of an increased oxide

content has been pointed out by Dhar. We thus see that in the case of the univalent cations, the decreasing sulphide content and the increasing oxide content in both the series (G and H) should produce respectively a stabilising and a sensitising action. This is in perfect agreement with the observed variation in the coagulating concentration which points to the action of two opposite effects as contemplated above. The results with barium chloride however go against the point of view of Dhar as both the decreasing sulphide content and the increasing oxide content should have a sensitising effect. Dhar and co-workers ignore the stabilising action of dilution resulting from an increase in the distance between the particles (or, in other words, the smaller number of particles per unit volume) pointed out by Mukherjee (*loc. cit.*) and Kruyt (*Kolloid Z.*, 1919, **25**, 1). It would appear however that the considerations advanced by Dhar do not account for the uniformly higher coagulating concentration of barium chloride, whereas the stabilising action of the increase in the distance does. Mukherjee and Sen (*loc. cit.*) pointed out that the behaviour on dilution is the result of two opposing effects namely, stabilisation consequent on an increase in the distance between the particles and sensitisation resulting from a diminution of the colloid—liquid interface. They also pointed out, in the absence of relevant data, that they are assuming that the particles do not change in any way as a result of the dilution. It has since been observed that the cataphoretic speed of particles of this sol decreases on dilution. Thus a smaller cataphoretic speed does not necessarily mean a sensitisation as observed with an increased oxide content. This contrast points again to the stabilising effect that dilution as such has. If this be recognised the uniformly higher coagulating concentration of barium chloride finds a sufficient explanation.

Dhar assumes that in view of the higher coagulating concentration of potassium chloride, chlorine ions are adsorbed to a greater extent on dilution. This has the effect of increasing the charge and of stablising the sol. He also points out that as the coagulating concentration of the barium chloride is low there is no such stablising action. There is only the sensitising action of a diminution in the interface consequent upon dilution (which was first pointed out by Freundlich) to be considered. The coagulating concentrations of potassium and barium chloride given in this paper are of about the same strength as observed by Dhar. This explanation therefore fails. It may be pointed out that dilution of the colloid in the

experiments of Dhar is least expected to increase the equilibrium concentration of the chlorine ions in the case of potassium chloride as the amount is assumed to be negligible in comparison to the total quantity of ions present. Of course, the nature of the interface may change. Further, a consideration of the fact that the sols used in this work have a different composition and that a diminution in the oxide content is responsible for the observed stabilisation also fails to account for the stabilisation against barium chloride observed in series G and H.

The effect of saturating with hydrogen sulphide a sol containing neither arsenious oxide nor hydrogen sulphide in excess and then driving the free hydrogen sulphide out by hydrogen was next studied. Two sols were prepared, one by the addition of hydrogen sulphide solution to a solution of arsenious oxide such that all the oxide was just converted into the sulphide without it being necessary to pass a stream of hydrogen sulphide gas through it. A portion of this sol, J, was tested and found to be free from excess of arsenious oxide or hydrogen sulphide. It was kept as usual in a Jena glass bottle with a black wrapper. Through a second portion a stream of hydrogen sulphide gas was passed for ten minutes after which the excess was removed by a stream of hydrogen (sol K). The coagulating concentrations were all determined in the same day.

TABLE VI.

HCl		KCl		LiCl		$BaCl_2$	
Sol J.	J/2.	J.	J/2.	J.	J/2.	J.	J/2.
0·037	0·042	0·053	0·066	0·061	0·08	0·0013	0·0015
Sol K.	K/2.	K.	K/2.	K.	K/2.	K.	K/2.
0·046	0·050	0·0063	0·075	0·074	0·093	0·00135	0·00155

Sol K shows greater stability than sol J including the case of barium chloride. The higher concentration of barium chloride is curious in view of the opposite observation of Mukherjee and Sen (*loc. cit.*, confirmed by Dhar and Ghosh, *loc. cit.*, *Kolloid Z.*) on half saturation with hydrogen sulphide. The amount of adsorbed and free hydrogen sulphide, which determines the nature and number of ions in the interfacial double layer, is probably different in the two cases and is responsible for this difference.

In view of the uniform stabilisation on dilution against coagulation by barium chloride observed in this paper, measurements of cataphoretic speeds (for procedure see Mukherjee and co-workers, *loc. cit.*) were made with one sol L prepared so as to contain neither excess of hydrogen sulphide nor of arsenious oxide. The results are given below. The speeds have been corrected for alterations in viscosity taking that for water as unity.

TABLE VII.

Sol L.

Conc. of potassium chloride	...	0	0·002	0·004	0·01	0·025	0·045
Cataphoretic speeds	...	67·6	50·5	54·7	53(?)	56·6	56·1
Conc. of barium chloride	...	0	0·0002	0·005	0·00067	—	0·00099*
Cataphoretic speeds	...	67·6	34·9	23·5	22	—	19·1

The speeds show variations similar to that observed before and on that ground it is difficult to account for the different behaviour against coagulation by barium chloride.

Summary.

(*a*) It has been observed that increasing concentrations of arsenious oxide sensitise the sol in keeping with the observed decrease in cataphoretic speeds.

(*b*) On the other hand, dilution diminishes the speed but stabilises the sol. This contrast cannot be accounted for on the basis of a change in the concentration of arsenious oxide but can best be accounted for by a consideration of the effects of dilution considered by Mukherjee and Sen (*loc. cit.*) and by Kruyt and Spek (*Kolloid Z.*, 1919, **25**, 1).

(*c*) The distinction between a normal and an abnormal behaviour on the basis of a difference in the coagulating concentrations is not justified.

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* Partial precipitation took place during measurement.

ERRATA

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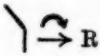
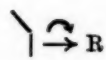
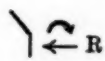
	,, Mechanism, 3 column 2.		
	,, Mechanism 4, column 2.		
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Synthesis in the Pyrazolone Series. Action of Semi- and Thiosemi-carbazides on Ketonic Esters. Part III.

By Satish Chandra De and Devendra Nath Dutt.

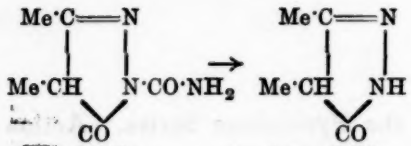
In previous communications (*J. Indian Chem. Soc.*, 1926, **3**, 30; 1928, **5**, 459) of this series it has been shown by one of us that thiosemicarbazide and semicarbazide condense with β-ketonic esters to form pyrazolone derivatives with carbothioamide and carbonamide groupings as substituents and that they have different degrees of stability. In Part II it has been shown that the behaviour of these carbazides towards benzoylacetic ester and diacetosuccinic ester differs from that of acetoacetic ester inasmuch as, instead of yielding the intermediate carbazones, they produce at once the pyrazolone compounds.

The object of the present investigation is to study the action of semi- and thiosemi-carbazides on the various substitution products of acetoacetic ester, namely, methylacetoacetic ester, ethylacetoacetic ester, dimethylacetoacetic ester, oxalacetic ester, benzoylacetoacetic ester, acetylacetoacetic ester and acetosuccinic ester; and it has now been found that the carbazides yield with the methyl-, ethyl- and dimethyl-acetoacetic esters pyrazolone compounds free from the carbothioamide or carbonamide group, due evidently to the looseness with which such groups are attached to the nucleus.

With the exception of methylacetoacetic ester the other esters show no tendency to unite with the carbazides at the ordinary temperature. From this ester and semicarbazide two products are formed (*vide* Experimental), and of these the lower melting substance is either a semicarbazone (I) or a pyrazolone carbonamide, (II) and the higher melting one is 3:4-dimethylpyrazolone:

$$CH_3\cdot CO\cdot CHMe\cdot CO_2Et + NH_2\cdot NH\cdot CO\cdot NH_2 \rightarrow \begin{matrix} CH_3\cdot C\cdot CH\cdot Me\cdot CO_2Et \\ \| \\ N\cdot NH\cdot CO\cdot NH_2 \end{matrix} \quad \text{or}$$

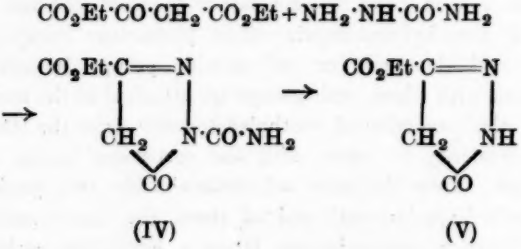
(I)



(m.p. 180°) (II) (m.p. 262°) (III)

With thiosemicarbazide methylacetoacetic ester gives a thiosemicarbazone which is relatively stable in warm water or alcohol but in boiling water is transformed into 3:4-dimethylpyrazolone which is derived evidently from the pyrazolone carbothioamide, first formed during the process. Thiosemicarbazide and semicarbazide give with dimethylacetoacetic ester the same compound, *viz.*, 4:4′-dimethylpyrazolone. Ethylacetoacetic ester yields with semicarbazide two products, *viz.*, 3-methyl-4-ethylpyrazolone-1-carbonamide and 3-methyl-4-ethylpyrazolone. This latter compound is also formed with thiosemicarbazide.

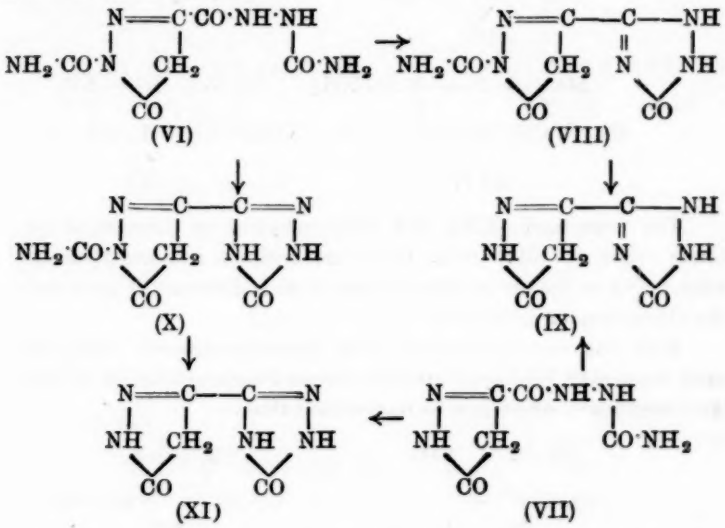
Oxalacetic ester reacts with semicarbazide in the usual manner to yield pyrazolone-3-carboxylic ester derived from pyrazolone-1-carbonamide-3-carboxylic ester first formed by the elimination of the carbonamide group.



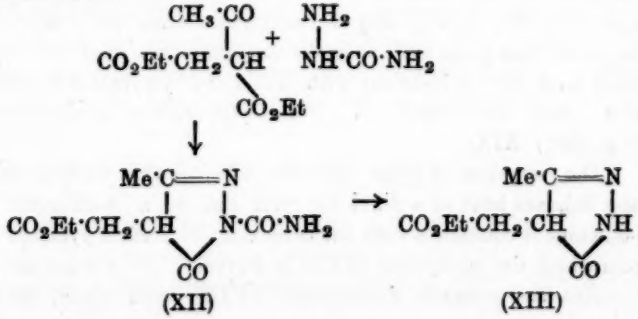
(IV) (V)

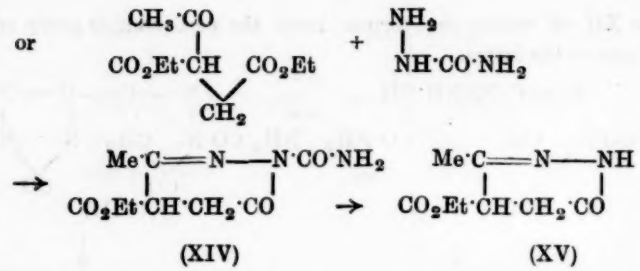
Along with pyrazolonecarboxylic ester another compound possessing the empirical formula, $C_5H_5O_2N_5$ has also been isolated the formation of which can be easily explained by supposing that semicarbazide acts upon the carboxylic ester group of either (IV) or (V) and the compound (VI or VII) so obtained then parts with a molecule of water and yields a compound (either VIII or X) or

(IX or XI) of which the former loses the carbonamide group and gives rise to the latter.



Acetosuccinic ester gives with semicarbazide a mixture of two products which are separable by means of boiling water, one being completely insoluble and the other soluble. The insoluble product melts at 225° and gives on analysis a very high percentage of nitrogen. The constitution of this compound has not yet been determined. The nature of the reaction and the composition of this will be described in a subsequent communication. The water-soluble product melts at 220° and has the composition, $C_8H_{12}O_3N_2$. The formation of this substance can be illustrated by either of the following schemes:

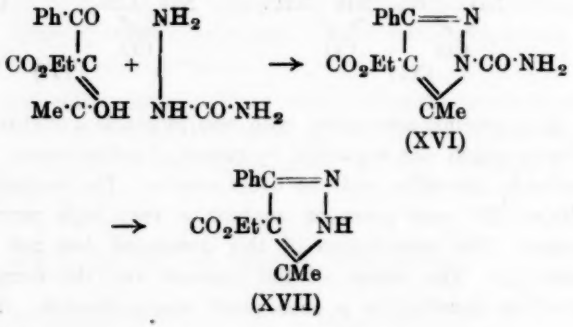




(XIV) (XV)

The compound (XIII) has been obtained by Curtius (*J. pr. Chem.*, 1894, **50**, 517) from hydrazine hydrate and acetylsuccinic ester. But as the compound obtained by us is different, it must have the alternative formula (XV).

Both the carbazides yield with benzoylacetoacetic ester the same compound 3-phenyl-5-methylpyrazole-4-carboxylic ester (XVII), the formation of which can be represented thus:

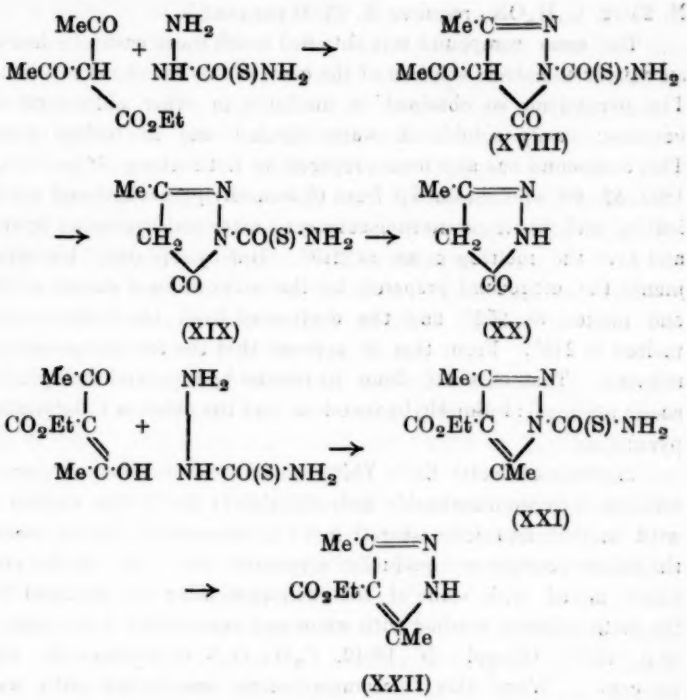


(XVI) (XVII)

But by condensation of acetylacetoacetic ester with semicarbazide two products are formed, *viz.*, 3:5-dimethylpyrazole-4-carboxylic ester (m.p. 96°) (XXII) and 3-methylpyrazolone (m.p. 215°) (XX). The same ester gives with thiosemicarbazide two products, one of which (m.p. 96°) is identical with 3:5-dimethylpyrazole-4-carboxylic ester and the other is 3-methylpyrazolone-1-carbothioamide (m.p. 180°) (XIX).

The formation of these products indicates that acetylacetoacetic ester behaves both as a β-ketonic ester and as a β-diketone. As a β-diketone it condenses with the carbazides to form a pyrazole (XXI) from which the compound (XXII) is derived. As a β-ketonic ester it yields the pyrazole derivatives (XVIII) from which the acetyl

group is probably eliminated giving the compound (XIX) and from this the compound (XX).



(XVIII)

(XIX)

(XX)

(XXI)

(XXII)

Experimental.

3:4-*Dimethylpyrazolone* (III).—Methylacetoacetic ester (1 mol.) dissolved in alcohol was added to an aqueous solution of semicarbazide hydrochloride (1 mol.) and sodium acetate (1 mol.). The mixture was allowed to stand overnight when only a small quantity of a solid product separated. After two days a further quantity of a solid crystalline product melting between 180° and 262° was obtained. It was dissolved in warm alcohol and the alcoholic solution fractionally precipitated with water, but these different fractions had the same melting point as the mother-substance. The mixture was then boiled with water for 3—4 hours with animal charcoal. From the filtrate a crystalline precipitate was obtained which melted at 262° with previous shrinkage at 249°. The melting

point remained unchanged even when it was crystallised four times from water. This substance was 3:4-dimethylpyrazolone. (Found: N, 25·12. $C_5H_8ON_2$ requires N, 25·00 per cent.).

The same compound was obtained much more easily by heating an aqueous-alcoholic solution of the components for about two hours. The pyrazolone so obtained is insoluble in ether, chloroform and benzene; easily soluble in warm alcohol and in boiling water. This compound has also been prepared by Rothenburg (*J. pr. Chem.*, 1895, **52**, 40) who obtained it from (*i*) 3-methylpyrazolone and methyl iodide, and (*ii*) from methylacetoacetic ester and hydrazine hydrate and gave the melting point as 249°. But by repeating his experiments the compound prepared by the latter method shrank at 249° and melted at 262°, and the compound from the former method melted at 249°. From this it appears that the two compounds are isomeric. That obtained from hydrazine hydrate and methylacetoacetic ester is 3:4-dimethyl-pyrazolone and the other is 1:3-dimethylpyrazolone.

Methylacetoacetic Ester Thiosemicarbazone.—When an aqueous solution of thiosemicarbazide hydrochloride (1 mol.) was shaken up with methylacetoacetic ester (1 mol.) in presence of sodium acetate, the thiosemicarbazone gradually separated out. The white precipitate mixed with some of the unchanged ester was decanted from the mother-liquor, washed with water and crystallised from alcohol, m.p. 192°. (Found: N, 19·42. $C_8H_{15}O_2N_3S$ requires N, 19·35 per cent.). When this thiosemicarbazone was boiled with water or when the reaction was carried out in boiling aqueous solution 3:4-dimethylpyrazolone was obtained.

3:4:4'-*Trimethylpyrazolone.*—A solution of semicarbazide hydrochloride (1 mol.) and sodium acetate (1 mol.) dissolved in the minimum quantity of water was poured into an alcoholic solution of dimethylacetoacetic ester. The mixture after being vigorously shaken for 3—4 hours was allowed to stand for two days with frequent shaking. As no solid separated out and the ester remained unchanged as an emulsion, the mixture was boiled for five to six hours when a clear solution was obtained which on cooling gave a crystalline solid. This was crystallised from water with the addition of animal charcoal, m.p. 262°-263°. (Found: N, 22·39. $C_6H_{10}ON_2$ requires N, 22·22 per cent.). The same compound was obtained with thiosemicarbazide.

3-*Methyl*-4-*ethylpyrazolone.*—Equal quantities of ethylacetoacetic ester, semicarbazide hydrochloride and sodium acetate were

heated in aqueous-alcoholic solution on the water-bath. Before all the ester (which was undissolved to begin with) went into solution, a white crystalline precipitate separated out after about 10 minutes and within a short time the reaction flask was filled with a voluminous flocculent precipitate. Heating was then continued for 20 minutes more, the solid was boiled with alcohol when a portion went into solution. From the filtrate, on cooling, a white light crystalline substance (m.p. 226°) was obtained and was found to be identical with 3-methyl-4-ethylpyrazolone of Rothenburg derived from hydrazine hydrate and ethylacetoacetic ester. (Found: N, 22·43. $C_6H_{10}ON_2$ requires N, 22·22 per cent.)

The same compound was obtained by heating an aqueous solution of thiosemicarbazide hydrochloride, sodium acetate and ethylacetoacetic ester for two to three hours.

3-Methyl-4-ethylpyrazolone-1-carbonamide.—The alcohol insoluble product in the above experiment consisted of white crystals, m.p. 258° (sharp). When this was boiled with water it gradually went into solution which on cooling gave 3-methyl-4-ethylpyrazolone, m.p. 226° (confirmed also by mixed melting point). As the substance could not be crystallised undecomposed and gave a very sharp melting point it was analysed. (Found: N, 24·62. $C_7H_{11}O_2N_3$ requires N, 24·85 per cent.).

3-(5-Keto-1:2:4-triazole)-pyrazolone (IX or XI).—This compound was obtained by heating a mixture of semicarbazide hydrochloride, oxalacetic ester and sodium acetate in molecular proportion in dilute alcoholic solution. After heating the mixture for 3—4 hours a white crystalline solid was obtained which could not be crystallised from any solvent; m.p. 265° (sharp). (Found: N, 42·10. $C_5H_5O_2N_5$ requires N, 41·90 per cent.).

Pyrazolone-3-carboxylic Ester (V).—The solution from the previous experiment gave on cooling a solid product which was dissolved in absolute alcohol and precipitated by ether as white needles, m.p. 178°. (Found: N, 17·84. $C_6H_8O_3N_2$ requires N, 17·04 per cent.).

3-Phenyl-5-methylpyrazole-4-carboxylic Ester (XVII).—To the alcoholic solution of benzoylacetoacetic ester (1 mol.) was added an aqueous solution of semicarbazide hydrochloride (1 mol.) and sodium acetate (1 mol.) and the mixture was heated for an hour. The precipitate was crystallised from water in white rectangular plates, m.p. 232°. The same compound was also obtained

when the semicarbazide was replaced by thiosemicarbazide. (Found: N, 12·36. $C_{13}H_{14}O_2N_2$ requires N, 12·17 per cent.).

3:5-Dimethylpyrazole-4-carboxylic Ester (XXII).—When a mixture of acetylacetoacetic ester (1 mol.) with an aqueous solution of semicarbazide hydrochloride and sodium acetate was heated for about an hour a semi-solid mass was obtained which became crystalline on long standing. When this solid was shaken up with ether a portion went into solution. The ether-insoluble product crystallised from alcohol, m.p. 215° and was identical with 3-methylpyrazolone. The solid obtained from the ethereal solution crystallised from alcohol, m.p. 96°, and was 3:5-dimethylpyrazole-4-carboxylic ester. (Found: N, 16·85. $C_8H_{12}O_2N_2$ requires N, 16·66 per cent.).

Two compounds were also obtained when the above experiment was repeated with thiosemicarbazide. But in this case 3-methylpyrazolone 1-carbothioamide (m.p. 180°) was formed together with the product melting at 96°, the method of separation and isolation being the same in both cases.

3-Methyl-2-keto-tetrahydro-pyridazine-4-carboxylic Ester (XV).—An alcoholic solution of acetoacetic ester (1 mol.) was added to an aqueous solution of semicarbazide hydrochloride (1 mol.) and sodium acetate. After heating the mixture for about 5 minutes white crystals began to separate out, heating being continued for nearly an hour. A portion of the precipitate on being boiled with water went into solution and gave on cooling a white crystalline precipitate, m.p. 220°. (Found: N, 15·00. $C_8H_{12}O_3N_2$ requires N, 15·22 per cent.).

The water-insoluble part consisted of white crystals which could not be crystallised from any ordinary organic solvent; m.p. 258° (decomp.).

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β-Diketones in Ring Formation. Part I.

By Umaprasanna Basu.

From a study on the condensation of certain β-diketones with cyanoacetamide, Bardhan (*J. Chem. Soc.*, 1929, p. 2223) claims that the methylene group of cyanoacetamide reacts with the keto-form of the dicarbonyl compound. But while investigating the behaviour of 2-acetyl*cyclo*hexanone and ethyl *cyclo*hexanone-2-carboxylate in several condensation reactions (Sen and Basu, *J. Indian Chem. Soc.*, 1927, **4**, 51; 1929, **6**, 309; 1930, **7**, 435), it was noticed that these reactions could be better represented by the enolic than the ketonic formula (*cf.* also Sen, *J. Chem. Soc.*, 1915, **107**, 1347). It was consequently considered to be of interest to examine critically the mechanism of the reaction of αγ-dicarbonyl compounds with cyanoacetamide.

At first it may be held that the initial product of such condensation would be an intermediate aldol (III), whether cyanoacetamide reacts with the enolic (I) or the ketonic form (II) of the dicarbonyl compound, thus:—

$$\left.\begin{array}{l} \underset{\text{(I)}}{\mathrm{R{\cdot}C(OH){=}CH{\cdot}CO{\cdot}R'}} \\ \text{or } \mathrm{R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R'} \\ \text{(II)} \end{array}\right\} + \mathrm{CN{\cdot}CH_2{\cdot}CO{\cdot}NH_2}$$

$$\longrightarrow \underset{\text{(III)}}{\mathrm{R{\cdot}C(OH){\cdot}CH_2{\cdot}CO{\cdot}R'}\ \mathrm{CN{\cdot}CH{\cdot}CO{\cdot}NH_2}} \longrightarrow \underset{\text{(IV)}}{\mathrm{R{\cdot}C{=}CH{:}CR'}\ \mathrm{CN{\cdot}C{\cdot}CO{\cdot}NH}}$$

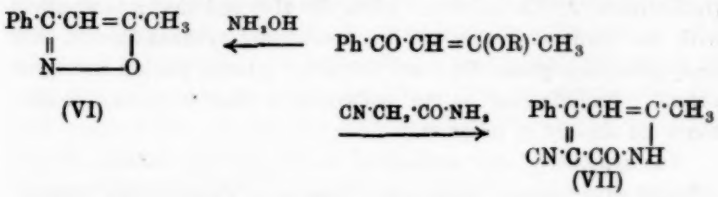
The intermediate aldol then readily passes into a pyridone derivative (IV) owing to the tendency for the formation of a six-membered ring. It is a difficult problem to distinguish between these two types of reaction, one a Michael and the other an aldol, as both are fundamentally additive in character. So the present investigation was

undertaken to determine the relative reactivities of the carbonyl group and the ethylenic linkage in β-diketones as indicated above.

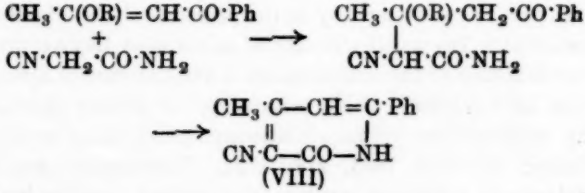
It is well-known that carbonyl groups are normally associated with a high reactivity towards sodium bisulphite, potassium cyanide, hydroxylamine, phenylhydrazine, and also substances containing a reactive methylene group, but are almost inert towards halogens, ozone, and potassium permanganate, whereas the ethylenic linkage readily responds to the latter reagents but show no appreciable reactivity towards the former ones. However in a system of the type —Ċ=CHX, that is, when an ethylenic linkage occurs in the α-position with respect to a so-called negative group (X=CO·R, CO_2Et etc.), its reactivity is considerably enhanced as shown by its behaviour even towards reagents of the former type (the ketonic reagents). A β-diketone when represented by the enolic formula (I) is a system of this type and as such it readily reacts with ozone, halogens, as well as with hydroxylamine, phenylhydrazine, etc. Hence it will not be unreasonable to expect a reactive methylene group to react with the ethylenic linkage present in the system. When, however, the ethylenic bond contains further a contiguous hydroxyl group (as in I), the presence of which enormously increases the additive capacity of the double linking (Meyer, *Annalen*, 1913, **398**, 66), a preferential addition at the ethylenic linkage becomes more probable. It is on such consideration, that the view hereinafter expressed is based, that is, the enolic phase of the β-diketone, being an αβ-unsaturated carbonyl compound, will readily undergo Michael reaction with the methylene group of cyanoacetamide (Michael, *Ber.*, 1894, **27**, 2126; Vorländer, *ibid.* p. 2053; *Annalen*, 1897, **294**, 267; Scheiber and Meisel, *Ber.*, 1915, **48**, 238; Thorpe and Norris, *J. Chem. Soc.*, 1921, **119**, 1201; Kon and collaborators, *J. Chem. Soc.*, 1923, **125**, 1361, and subsequent papers). This has been found to be the case as acetylacetone and ethyl acetylpyruvate readily condense with sodiocyanoacetamide to give rise to products identical with those obtained from cyanoacetamide by Bardhan, using Knoevenagel's reagent (*cf.* also Sen and Basu, *loc. cit.*). That a trace of sodium ethoxide (as distinct from molecular quantities of it) has been found to bring about the same condensation, further proves the fundamental identity of Michael and aldol reactions.

Next an *O*-ether (V) (Claisen, *Ber.*, 1907, **40**, 3903) of benzoylacetone in which the ethylenic bond is fixed was prepared and its reaction with cyanoacetamide studied. The above *O*-ether reacts

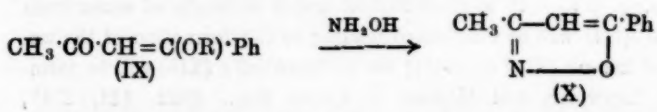
with hydroxylamine (a ketonic reagent) to give rise to 3-phenyl-5-methyl-*iso*oxazole (VI) (Claisen, *Ber.*, 1926, **59**, 144) as follows:



Accordingly cyanoacetamide (also a ketonic reagent) may react to form 3-cyano-4-phenyl-6-methyl-2-pyridone (VII). But on condensing the ether (V) with cyanoacetamide, the product isolated was not (VII) but its isomer 3-cyano-4-methyl-6-phenyl-2-pyridone (VIII), m.p. 310°, the formation of which may be represented in the following way:



Thus it would appear that though a substance containing a reactive methylene group be a ketonic reagent, it preferentially attacks the ethylenic linkage present in systems represented above*. This was further proved by isolating the pyridone derivative (VII), m. p. 275°-276°†, by conducting the same reaction with an isomeric ether (IX) which again normally reacts with hydroxylamine yielding 5-phenyl-3-methyl*iso*oxazole (X) (Claisen, *loc. cit.*).



* The formation of isomeric pyridones (VII and VIII) from benzoylacetone itself (Bardhan, *loc. cit.*) does not militate against the present hypothesis of preferential condensation at the ethylenic linkage as it is quite conceivable that the enolic phase is at one time set up next to the phenyl group and at another next to the methyl group.

† Issoglio (*Atti. R. Accad. Sci. Torino*, 1905, **40**, 495) who obtained a mixture of the pyridone derivatives (VII and VIII) by condensing benzoylacetone with ethyl cyanoacetate in presence of ammonia found the main product (VIII, yield 75%)

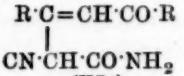
The constitution of the compound (VII) is proved from the facts that on hydrolysis it gives the known 4-phenyl-6-methyl-2-pyridone (Ruhemann, *J. Chem. Soc.*, 1899, **75**, 413) and that it is identical with the compound obtained by condensing cyanoacetamide with acetylphenylacetylene $Ph{\cdot}C{\equiv}C{\cdot}CO{\cdot}CH_3$ (Barat, *private communication*). Experiments on the behaviour of other *O*-ethers of β-diketones are already in progress.

The hypothesis was attempted to be critically examined from a different experimental standpoint altogether. Thus the two isomeric *C*-methyldibenzoylmethanes (the ketonic and enolic) were prepared and the condensation of cyanoacetamide with each of them was effected in the presence of Knoevenagel's reagent in aqueous—alcoholic solution as usual. In both cases the identical reaction product was isolated. This is only to be expected as in solution these isomers lose their structural individuality giving rise to an equilibrium mixture of the two isomers specially in the presence of the alkaline reagent employed. The small quantity of material at disposal precluded the investigation of the condensation in the presence of hydrogen chloride (an acid reagent) which admittedly is capable of bringing about the condensation between a carbonyl group and a methylene group (Claisen *Annalen*, 1883, **218**, 172). This however was tried with acetylacetone when no condensation product could be isolated showing thereby the inactivity of the carbonyl under such conditions and pointing to the enormous change in reactivity occasioned by enolising agencies. It should be noted here that the influence of enolising (benzene) or ketonising (alcohol) solvent does not alter the course of reaction pointing once again to the inherent tendency of such reactions to follow the course indicated above.

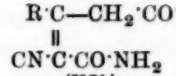
A passing reference may now be made as to the closure of the pyridone ring (IV). It is clear that at first a molecule of water from the aldol (III) will be eliminated leading to the formation of the unsaturated ketone (XI*a*) or (XI*b*); but preferentially (XI*b*) will be formed (*cf.* Lapworth and McRae, *J. Chem. Soc.*, 1922, **121**, 2747; also Kon, *loc. cit.*). The formation of (XI*b*) is further evident from

to melt at 310° and the isomer (VII) to melt at 263°-264°. Bardhan (*loc. cit.*) again records the melting point of the latter as 249°. These different statements led the author to repeat the condensation of benzoylacetone with cyanoacetamide when it was found that through the pyridone derivative (VIII) may be easily obtained in nacreous plates, m.p. 310°, it is very difficult to obtain the isomeric compound (VII) in a pure condition.

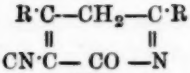
the fact that acetylenic ketones ($R{\cdot}C{\equiv}C{\cdot}CO{\cdot}R$) with cyanoacetamide give rise to condensation products similar to (IV) (Barat, *loc. cit.*). Next the amido-group present in (XI*b*) favours the formation of a dihydropyridone ring (XIII) as evident from the isolation of a compound (XIV) by Sen (*loc. cit.*). But it readily loses a molecule of water to give rise to the usual ring (IV). That the structure of the final compound is (IV) and not (XII) is confirmed by the synthesis



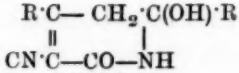
(XI*a*)



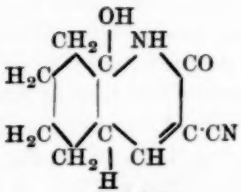
(XI*b*)



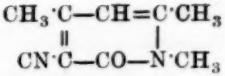
(XII)



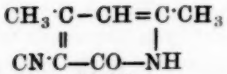
(XIII)



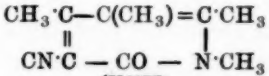
(XIV)



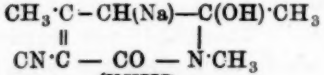
(XV)



(XVI)



(XVII)



(XVIII)

of 3-cyano-1:4:6-trimethyl-2-pyridone (XV) from acetylacetone and cyanoacetmethylamide (*cf.* Guareschi, *Atti. R. Accad. Sci. Torino*, 1893, **28**, 330, 837).

In ascertaining the position of the sodium in the Michael condensation product from acetylacetone and sodiocyanoacetamide, certain interesting observations were made. Thus on methylation it yielded 3-cyano-1:4:6-trimethyl-2-pyridone (XV) which indicates that it is the *N*-sodium salt of (XVI). Consequently the reaction between

acetylacetone and cyanoacetmethylamide was studied according to Michael's method when the condensation product (XV) was directly isolated. However, on conducting the same reaction in benzene suspension, an additive sodium compound was obtained which readily dissolved in water to give rise to (XV) and yields 3-cyano-1:4:5:6-tetramethyl-2-pyridone (XVII) on methylation. This indicates that the structure of the initial sodium compound is of the type (XVIII) (*cf.* Thorpe, *Proc. Chem. Soc.*, 1912, 51). The constitution of (XVII) was further confirmed by its synthesis from methylacetylacetone, $CH_3 \cdot CO \cdot CHMe \cdot CO \cdot CH_3$ and cyanoacetmethylamide.

The difference in the position of the sodium in Michael condensation products, as indicated above, may be taken as the primary reason for seeking a more scientific explanation of Michael's reaction itself. Then again the capacity of a trace of sodium ethoxide or alkali to cause the same type of reaction (*loc. cit.*) as brought about by molecular quantities of sodium, strengthens the ground for concluding that the hitherto accepted function of the sodium atom to explain the Michael's reaction is not of any fundamental consequence. On the other hand, the real explanation of such reactions is to be sought for in the development of electrical centres in the reacting molecules due no doubt to the influence of catalysts. All these points find expression in the theory propounded by Ingold (*J. Chem. Soc.*, 1926, **128**, 1868; *cf.* also Ingold, *J. Chem. Soc.*, 1930, p. 184). It may be held that prior to the commencement of reaction a reactive electrical centre equivalent to a sort of ionisation is developed in both the reactants by virtue of the catalyst. Thus the cyanoacetamide molecule is ionised and the negative ion (XIX) is attracted to the carbon atom marked with an asterisk in (XX) (the β-diketone molecule), "possessing a minute positive charge owing to the pull of the negative acyl group on the C=C electrons." Then (XXI) will represent the ion of the additive compound which then gives rise to the ion (XXII) of the condensation product with the elimination of two molecules of water. It is clear from (XXII) that when sodiocyanoacetmethylamide is condensed with acetylacetone or methylacetylacetone,

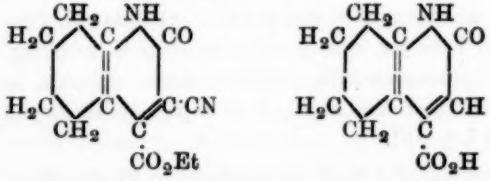
$$CN \cdot \overset{-}{C}H \cdot CO \cdot NH_2 \quad + \quad HO \cdot \overset{*}{C} = C - C = O \longrightarrow$$

(XIX) (XX)

(XXI) (XXII)

the respective pyridone derivatives (XV) and (XVII) are directly obtained as in these cases there is no chance for the formation of the ion (XXII) of the condensation product.

Finally the condensation between ethyl *cyclo*hexanone-2-oxalate and cyanoacetamide is being studied in order to find whether this β-diketone yields a mixture of quinoline and *iso*quinoline derivatives or one single component. A compound melting at 214-215° and appearing to have the formula $C_{13}H_{14}O_3N$, was obtained and this on hydrolysis with fuming hydrochloric acid gave an acid, m. p. 309°. But the acid could not be converted into a simple tetrahydroquinoline derivative by heating. However, from the sharp melting point and the behaviour of cyanoacetamide on ethyl acetylpyruvate the compound may be regarded as ethyl 3-cyano-5:6:7:8-tetrahydro-2-quinolone-4-carboxylate (XXVIII) and the acid as 5:6:7:8-tetrahydro-2-quinolone-4-carboxylic acid (XXIX).



(XXVIII) (XXIX)

Experimental.

Condensation of O-*Ethylbenzoylacetone*, $Ph{\cdot}CO{\cdot}CH{=}(OEt){\cdot}CH_3$ *with Cyanoacetamide*: *Formation of* 3-*Cyano*-4-*methyl*-6-*phenyl*-2-*pyridone* (VIII).—The ethyl ether was prepared according to Claisen's method (*loc. cit.*) and obtained as an oil with a pleasant odour, b. p. 155-157°/11 mm. An alcoholic solution of the oil (3 g.) was gradually added with shaking to a suspension of sodiocyanoacetamide prepared from 1·3 g. of cyanoacetamide in hot alcohol, and 0·35 g. of sodium also dissolved in absolute alcohol. The colour of the mixture became deeper and it was left aside. After 2 days the

hard globular sodium salt was collected, dissolved in warm water and the solution acidified when the condensation product (2 g.) was isolated. Another crop (0·8 g.) was obtained on acidulation of the mother-liquor. Crystallising the crude product (m. p. 303-306°) from glacial acetic acid with the addition of a few drops of water, 3-cyano-6-phenyl-4-methyl-2-pyridone was obtained, m.p. 310°, darkening earlier (Issoglio, *loc. cit.*). (Found: N, 13·40. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.).

The same compound may be obtained by condensing the ether with cyanoacetamide in the presence of diethylamine as follows: Cyanoacetamide (1·3 g.) was dissolved in water by warming and the ether (3 g.) added, with just enough alcohol to effect a clear solution. About 1 c. c. of diethylamine was added and the solution was heated on a water-bath for about 45 minutes when crystals began to separate. The flask was then left overnight. Next day 3-cyano-6-phenyl-4-methyl-2-pyridone was isolated in an yield nearly equal to that obtained by Michael's reaction.

Hydrolysis of the above Pyridone Derivative.—The substance was heated with sulphuric acid (80%) for about an hour. The cooled mixture was poured into water and filtered. The filtrate on neutralisation with sodium carbonate gave a solid which on crystallisation from alcohol melted at 182-183°. (Found: N, 7·8. $C_{12}H_{11}ON$ requires N, 7·57 per cent.). It was soluble in boiling water, gave a crimson colouration with alcoholic ferric chloride, and possessed all the characteristics ascribed to 6-phenyl-4-methyl-2-pyridone by Bardhan (*loc. cit.*).

Condensation of O-*Methylbenzoylacetone* $Ph{\cdot}C(OMe)=CH{\cdot}CO{\cdot}CH_3$ *with Cyanoacetamide: Formation of* 3-*Cyano*-4-*phenyl*-6-*methyl*-2-*pyridone* (VII).—*O*-Methylbenzoylacetone was prepared from benzalacetone dibromide according to the method described by Weygand (*Ber.*, 1925, **58**, 1473) and was obtained as an yellow oil, b.p. 147-148°/11 mm. To a cooled alcoholic suspension of sodiocyanoacetamide obtained from cyanoacetamide (4 g.) and sodium (1 g.), the ether (8 g.) was gradually added without allowing the temperature to rise. The mixture was left over for 3 days with occasional shaking. Carbon dioxide was then passed into the mixture and the precipitate was filtered and washed with water. The residue (3 g.) on crystallisation from alcohol melted at 275-76° sintering and darkening a few degrees earlier (yield, 30%). (Found: N, 13·37. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.). On repeated crystallisation

from acetic acid it was obtained in colourless prismatic needles melting at the same temperature. A mixture of this with the isomeric compound 3-cyano-6-phenyl-4-methyl-2-pyridone (m.p. 310°) melted at 247°. It dissolves in alkali but is precipitated unchanged on acidulation. It is also soluble in boiling water and acetone and imparts no colouration to alcoholic ferric chloride. The pyridone is soluble in concentrated sulphuric acid but is precipitated unchanged on dilution.

Hydrolysis : *Formation of 4 Phenyl-6-methyl-2-pyridone.*—The above condensation product was heated with 80% sulphuric acid for more than half an hour. On cooling crystals began to separate when water was added, and the product on crystallisation from dilute alcohol (charcoal) was obtained in colourless needles, m.p. 206-207° (Ruhemann, *loc. cit.*) not depressed by admixture with the compound obtained by hydrolysing 3-cyano 4-phenyl-6-methyl-2-pyridone from the condensation product of benzoylacetone described below. (Found : N, 7·9. $C_{12}H_{11}ON$ requires N, 7·6 per cent.).

Condensation of Benzoylacetone with Cyanoacetamide.—Owing to the reason already stated, the condensation with diethylamine as the condensing agent, was effected in dilute alcohol and from the reaction mixture the main product, 3-cyano-6-phenyl-4-methyl-2-pyridone (VIII), m.p. 310° was easily isolated. Next day the mother-liquor, on acidification, yielded a product, m.p. 245-247° which was partly soluble in alcohol. The insoluble portion mainly consisted of 3-cyano-6-phenyl-4-methyl-2-pyridone whereas the crystals from the alcoholic solution melted indifferently between 248° and 255°. On recrystallisation from boiling water in which it was difficultly soluble, it melted at 263-264° (*cf.* Issoglio, *loc. cit.*). The melting point is raised to 273° when admixed with the compound (m.p. 275-76°) previously described. The crop, m.p. 248-255°, however, on hydrolysis with concentrated sulphuric acid (80%) yields 4-phenyl-6-methyl-2-pyridone, m.p. 206-207°, as found by Bardhan.

Condensation of Methyldibenzoylmethanes, Ph·CO·CHMe·CO·Ph *and* Ph·CO·CMe=C(OH)Ph, *with Cyanoacetamide: Formation of 3-Cyano-4:6-diphenyl-5-methyl-2-pyridone.*—Both the methyldibenzoylmethanes were prepared from dibenzoylmethane (Diekmann, *Ber.*, 1922, **55**, 2481). The ketonic form is more soluble in alcohol and imparts no colouration to ferric chloride solution, whereas the enol is difficultly soluble in alcohol and gives the characteristic violet colouration with ferric chloride. The two ketones (3 g. each)

were separately dissolved in alcohol and an aqueous solution of cyanoacetamide (1·1 g.) was added to each solution with sufficient alcohol to effect a clear solution. Diethylamine (4 c. c.) being added to each, they were heated under reflux on the water-bath for about 12 hours, when on acidification both the mixtures yielded the same pyridone derivative, almost in equal yield. Crystallising from pyridine with the addition of a few drops of water, it was obtained in beautiful colourless plates, m.p. 304-305°. (Found: C, 79·4; H, 5·1; N, 9·7. $C_{19}H_{14}ON_2$ requires C, 79·7; H, 4·89; N, 9·8 per cent.). The pyridone is soluble in warm alkali; and forms a crystalline sodium salt. Ferric chloride imparts no colouration to its alcoholic solution. Concentrated sulphuric acid dissolves it but on dilution with water it is precipitated unchanged. This is converted by the action of sulphuric acid (80%) into 4:6-diphenyl-5-methyl-2-pyridone which crystallises in needles from dilute alcohol, m.p. 263-264°. The latter is soluble in warm alkali and forms a crystalline sodium salt. In alcoholic solution it imparts a red colouration to ferric chloride. (Found: N, 5·65. $C_{18}H_{15}ON$ requires N, 5·36 per cent.).

Condensation of Dibenzoylmethane and Cyanoacetamide: Formation of 3-Cyano-4:6-diphenyl-3-pyridone (IV, R = Ph).—The β-diketone was prepared according to the method of Claisen (*Annalen*, 1896, **291**, 52) from ethyl benzoate and acetophenone, m.p. 77-78°.

An equimolecular mixture of the β-diketone and cyanoacetamide in alcoholic solution was heated with a few drops of piperidine on the water-bath for about 3 hours, and left overnight. Next morning on acidifying the clear solution the pyridone derivative was isolated in an yield of about 40%. It crystallised from pyridine with the addition of a few drops of alcohol in colourless needles, m.p. 318-320°. (Found: C, 79·25; H, 4·7; N, 10·0. $C_{18}H_{12}ON_2$ requires C, 79·41; H, 4·4; N, 10·29 per cent.). The substance is soluble in glacial acetic acid but difficultly so in other organic solvents. It also dissolves in alkali and in concentrated sulphuric acid from which solutions it can be recovered unchanged on acidification and on dilution with water respectively.

Hydrolysis: Formation of 4:6-Diphenyl-2-pyridone.—On hydrolysing the above cyanopyridone with sulphuric acid (80%) 4:6-diphenyl-2-pyridone was obtained in fine slender needles from dilute alcohol (charcoal), m.p. 207-208°. It is soluble in warm alkali and imparts a red colouration to an alcoholic solution of ferric chloride.

(Found: N, 5·8. $C_{17}H_{13}ON$ requires N, 5·66 per cent.) (*cf.* Meyer, *J. pr. Chem.*, 1914, *ii*, **90**, 1).

Condensation of Ethyl Acetylpyruvate with Cyanoacetamide.—This reaction has been studied by Bardhan (*loc. cit.*). Here the condensation in benzene suspension is described. Sodiocyanoacetamide prepared in the usual way was filtered, washed with cold absolute alcohol, anhydrous ether, and dried in *vacuo*. It was shaken in benzene suspension with molecular proportion of ethyl acetylpyruvate for about 2 to 3 hours and then left overnight. Next morning the benzene layer was decanted off and the sodium salt of the condensation product formed was dissolved in water. On acidifying the yellow solution ethyl 3-cyano-6-methyl-2-pyridone-4-carboxylate was obtained which on crystallisation from glacial acetic acid melted at 218°. It was also soluble in boiling water and alcohol.

The condensation may also be effected by adding the ketonic ester to cyanoacetamide itself in benzene suspension in presence of piperidine.

The hydrolysis product, 6-methyl-2-pyridone-4-carboxylic acid, may be obtained by heating the condensation product with caustic soda solution (30%) for about 3 hours. The acid is soluble in boiling water, dilute acetic acid, and concentrated sulphuric acid with a green fluorescence. It begins to darken at about 270° but does not melt even at 325°. On concentrating its aqueous solution in *vacuo* over sulphuric acid long prismatic plates with a slight yellow tinge were formed which were washed with alcohol and dried in *vacuo*. (Found: N. 8·6. $C_7H_7O_3N$, H_2O requires N, 8·2 per cent.). On heating the dry substance in a test tube, water was found to condense on the cooler part. If however the compound be rapidly heated in an electric bath or dipped into hot sulphuric acid it melts at 225-226° to a red liquid.

Condensation with Acetylacetone: (*i*) *Formation of 3-cyano-4: 6-dimethyl-2-pyridone* (XVI).—Cyanoacetamide (1·7 g.) dissolved in alcohol was added to an alcoholic sodium ethoxide (0·5 g. Na). The sodium salt was rapidly filtered, washed with alcohol and ether and dried in *vacuo*. To the sodium salt suspended in anhydrous benzene, acetylacetone (2 g.) was added with shaking. Next day the benzene layer was decanted off and on adding water and acidifying the clear solution, the known pyridone derivative, m.p. 288-89° (Guareschi, *loc. cit.*) was obtained. The condensation may also be effected in alcoholic solution using molecular sodium (Michael's method) or a trace of sodium ethoxide (2% solution) as the condensing agent.

(*ii*) *Attempt to condense by means of Hydrochloric Acid.*—Dry hydrogen chloride (3 g.) was passed into a cooled solution of acetylacetone (1 g.) and cyanoacetamide (1 g.) in dilute alcohol. No appreciable change was observed and no condensation product could be isolated from the reaction mixture even after a fortnight. The solution was then carefully neutralized, when on adding a trace of diethylamine the solution became warm and turned red. Soon crystals (1·5 g) of the lutidostyril derivative, m.p. 288°, separated out.

(*iii*) *Formation of 3-Cyano-1 : 4 : 6-trimethyl-2-pyridone* (XV).—(*a*) *By Methylating the Michael Sodium Salt.* The sodium salt formed by conducting the above reaction in alcoholic solution was filtered, washed with cold alcohol and ether and dried in *vacuo*. It (4·5 g.) was heated with methyl iodide (10 g.) and methyl alcohol (10 c.c.) in a sealed tube at 105-110° for 3 hours. Beautiful stout crystals that separated on crystallisation from alcohol melted at 203-204°. It was insoluble in alkali. (Found: N, 17·3. $C_9H_{10}ON_2$ requires N, 17·28 per cent.).

(*b*) *By Condensing with Cyanoacetmethylamide.*—Cyanoacetmethylamide was prepared by shaking ethyl cyanoacetate (30 g.) with an ounce of methylamine (33% solution) under cooling. The clear solution on concentration over sulphuric acid in *vacuo* yielded the amide (20 g.) in well crystalline form. Crystallising from ethyl alcohol it melted at 104°. (Found: N, 28·65. $C_4H_6ON_2$ requires N, 28·57 per cent.).

On adding a few drops of piperidine to a clear solution of acetylacetone (1·8 g.) and cyanoacetmethylamide (1·8 g.), the solution became warm and the colour changed to deep yellow. On keeping in a warm place (40-50°), fine crystals began to separate when it was left overnight at ordinary temperature. Next day the beautiful shining crystals (2·5 g.) were collected. They were insoluble in alkali, gave no colouration with ferric chloride, and were soluble in alcohol and boiling water; m.p. 203-204°, which was not depressed by addition of the product described under (*a*).

The pyridone derivative was directly obtained when the same reaction with sodiocyanoacetmethylamide was conducted in alcoholic solution.

The condensation was also carried out in benzene suspension in the following way: The sodium salt (2 g.) of the amide prepared and dried in the usual way, was taken in anhydrous benzene suspension and shaken with acetylacetone (1·7 g.). Within an hour a heavy

granular sodium compound was formed. After two days the sodium salt (3·4 g.) was collected, washed with anhydrous ether and taken in water in which it readily dissolved, but soon crystals separated out and these were found to be 3-cyano-1:4:6-trimethyl-2-pyridone (XV).

(*iv*) *Formation of* 3-*Cyano*-1:4:5:6-*tetramethyl*-2-*pyridone* (XVII) —The sodium salt obtained by condensing acetylacetone with sodiocyanoacetmethylamide in benzene suspension was dried in *vacuo* and heated with twice the required quantity of methyl iodide in anhydrous benzene suspension in a sealed tube at 100° for about 3 hours. The clear benzene layer was decanted off. The residual viscous mass was taken in water in which it was completely soluble. On making the solution alkaline fine silky needles separated out which on crystallisation from water melted at 179-180° and was found to be identical with the compound obtained by condensing cyanoacetmethylamide with methylacetylacetone described afterwards.

Condensation with Methylacetylacetone: (*i*) *Formation of* 3-*cyano*-4:5:6-*trimethyl*-2-*pyridone*.—The condensation product was obtained from methylacetylacetone and cyanoacetamide in alcoholic solution in presence of a few drops of piperidine, the yield being 75%. Crystallising from alcohol it was obtained in needles, m.p. 305-306° (Guareschi, *loc. cit.*). (Found: N, 17·45. $C_9H_{10}ON_2$ requires N, 17·28 per cent.). It is soluble in alkali, and is precipitated unchanged on acidification.

(*ii*) *Formation of* 3-*Cyano*-1:4:5:6-*tetramethyl*-2-*pyridone* (XVII) —The product obtained by condensing the β-diketone with cyanoacetmethylamide in the usual way crystallises from boiling water in fine silky needles, m.p. 180°. (Found: N, 16·15. $C_{10}H_{12}ON_2$ requires N, 15·9 per cent.). It was soluble in alcohol and in other common solvents but insoluble in alkali.

Conducting the reaction with sodiocyanoacetmethylamide in alcoholic solution (Michael's reaction) 3-cyano-1:4:5:6-tetramethyl-2-pyridone was directly obtained.

Condensation of Ethyl cyclo*Hexanone*-2-*oxalate with Cyanoacetamide*: *Formation of Ethyl* 3-*Cyano*-5:6:7:8-*tetrahydro*-2-*quinolone*-4-*carboxylate* (XXVIII).—A clear solution of cyanoacetamide (2·2 g.) in water and ethyl *cyclo*hexanone-2-oxalate (5·5 g.) (Kötz and Michaels, *Annalen*, 1906, **350**, 210) in alcohol with the addition of piperidine (2 c.c.) was warmed at 60° for 2 hours when the yellow crystals

separated (1·5 g.) were collected. After adding a few more drops of piperidine to the mother-liquor it was left overnight. On acidification another crop (1·8 g.) was obtained. It crystallised from boiling amyl alcohol (charcoal), m.p. 214-215°. (Found: N, 11·6. $C_{13}H_{14}O_3N_2$ requires N, 11·39 per cent.). The quinolone derivative is partly soluble in alcohol and acetic acid but readily dissolves in concentrated acids and in alkalis from which it may be obtained unchanged on dilution with water and acidification respectively. Its alcoholic solution imparts no colouration to ferric chloride but exhibits a beautiful emerald green fluorescence.

Hydrolysis: Formation of 5:6:7:8-*Tetrahydro-2-quinolone-4-carboxylic Acid* (XXIX).—The above condensation product (2 g.) was heated with fuming hydrochloric acid (14 c.c.) at 170-180° for about 4 hours. Stout crystals separated. The solid obtained on neutralising the hydrochloric acid with sodium carbonate, was crystallised from dilute acetic acid. Recrystallising from the same solvent (charcoal) it was obtained in clusters of needles, m.p. 308°, sintering earlier. (Found: N, 7·4. $C_{10}H_{11}O_3N$ requires N, 7·25 per cent.). The substance is soluble in alcohol, in alkali and also in sodium carbonate solution with effervescence, but is reprecipitated on acidification from the latter solution. The carbonyl group cannot be removed by heating the substance to its melting point as the acid itself began to decompose at that condition.

In conclusion, I wish to express my grateful thanks to Professor H. K. Sen, for his kind interest in this investigation.

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Colour of Complex Diazoles. Part IV. Constitution of Thiele's Supposed *o*-Benzylene-1 :3-benziminazole.

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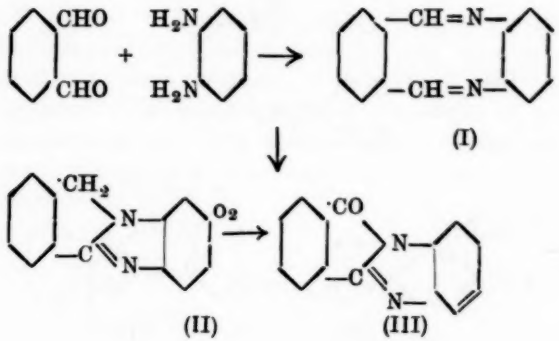
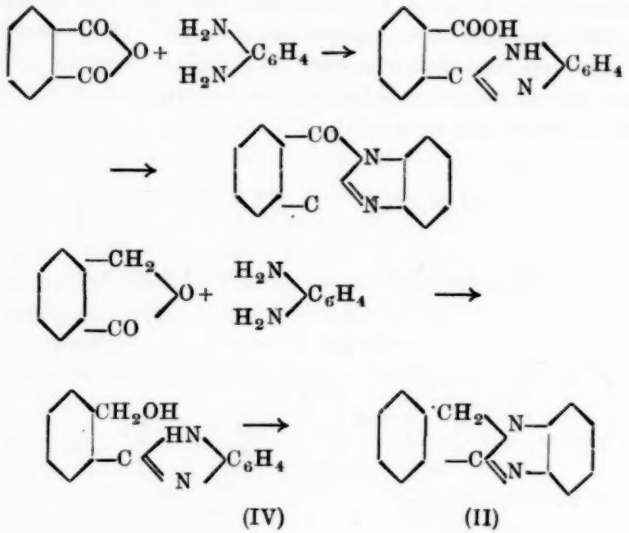
In connection with our investigation upon the absorption spectra of various condensed iminazoles, it became necessary to prepare a quantity of *o*-benzylene-1 :3-benziminazole. This compound has been synthesised by Thiele and Falk (*Annalen*, 1906, **347**, 112) by condensing phthalaldehyde with *o*-phenylene diamine. They described it as a colourless crystalline compound, m.p. 210°. Normally the reaction mentioned above would lead to the formation of a condensed eight-membered ring system (I).



But Thiele and Falk assigned the formula (II) to the product of this reaction, because, on oxidation with permanganate it easily changed into *o*-benzoylenebenziminazole (III), a compound of definite constitution. But in spite of this strong evidence in support of formula (II) it is difficult to comprehend how an atom of hydrogen from one methine group in the compound (I) travels over to the other methine group, converting the latter into a methylene group as in the compound (II). There is no reason why such a hydrogen atom should be labile. These facts led us to synthesise *o*-benzoylenebenzi-

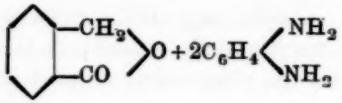
minazole by a method which would leave no doubt as regards its constitution.

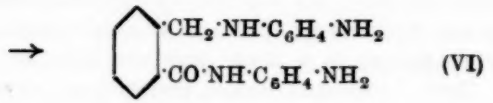
It is now well known that ketonic condensed iminazoles like (III) can be very easily prepared by fusing the anhydrides of dibasic acids with diamines or by boiling them in absolute alcoholic solutions (Bistrzycki and Lecco, *Helv. Chim. Acta*, 1921, **4**, 425; Bistrzycki and Fässler, *ibid*, 1923, **6**, 521; Chakravarti, *J. Indian Chem. Soc.*, 1924, **1**, 18; Chakravarti and Sen-Gupta, *ibid*, 1925, **1**, 330). In a similar manner we supposed that the condensation between phthalide and *o*-phenylene diamine would lead to the formation of the compound (II) according to the following general scheme: —



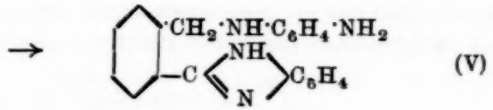
(IV) (II)

But when phthalide was fused with *o*-phenylene diamine a compound, m.p. above 300°, which is proved to be benziminazole-2-benzyl-*o*-phenylene diamine (V) containing four nitrogen atoms was obtained. Evidently two molecules of the diamine had condensed with one of the phthalide. On boiling together the phthalide and the diamine another product, m.p. 162° (VI), also containing four nitrogen atoms resulted. This, on fusion, lost a molecule of water and was converted into (V). Hence the reactions take the following course:



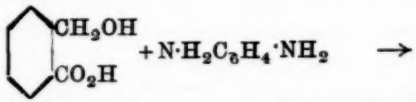


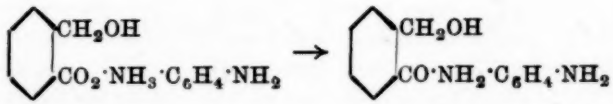
(VI)



(V)

On treating *o*-oxymethylbenzoic acid with *o*-phenylene diamine in the presence of 4*N*-hydrochloric acid, following a method similar to that of Phillips (*J. Chem. Soc.*, 1928, p. 2398), benziminazole-2-*o*-oxymethylbenzene (IV) and benziminazole-2-benzyl-*o*-phenylene diamine (V) were obtained. But the yield of the desired compound (IV) was extremely poor. Next, when we treated *o*-oxymethylbenzoic acid with the diamine in cold absolute alcohol, we obtained an addition compound *o'*-aminophenylammonium-*o*-oxymethylbenzoate (VII) which contained two atoms of nitrogen. On boiling this compound with absolute alcohol it lost a molecule of water and was converted into *o*-oxymethyl-*o'*-aminobenzanilide (VIII) as follows:—





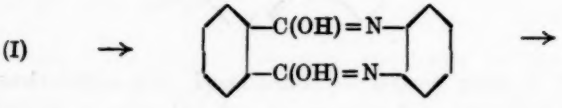
(VII) (VIII)

The condensation of phthalide and the diamine in cold absolute alcohol also gave the compound (VIII) in good yield.

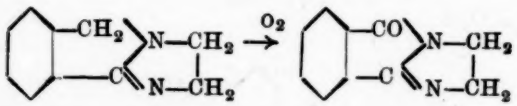
The dehydration of *o*-oxymethyl-*o'*-aminobenzanilide with acetic anhydride or by fusion, yielded *o*-benzylene-1:3-benziminazole (II)

in colourless crystalline rosettes, m.p. 185°. This compound also, on oxidation, gave *o*-benzoylene-1:3-benziminazole (III).

It is therefore evident that the constitution assigned by Thiele and Falk (*loc. cit.*) to their compound is erroneous; because on dehydration, compound (VIII) can be converted only into compound (II). For comparison we prepared Thiele and Falk's compound. The purest sample showed m.p. 213·5° and not 210° as mentioned by them. Their compound cannot therefore be represented by formula (II), but must be given the alternative formula (I). Its oxidation to *o*-benzoylene-1:3-benziminazole (III) can be easily explained even on the basis of this constitution:—



We further succeeded in bringing about the condensation of phthalide with ethylene diamine in cold absolute alcohol and the resulting product was easily converted into *o*-benzylene-dihydroiminazole (X) which on oxidation gives *o*-benzoylene dihydroiminazole (XI).



(X) (XI)

Experimental.

Condensation of Phthalide with o-Phenylene Diamine by Fusion.—Phthalide (9·7 g.) and *o*-phenylene diamine (4·3 g.) were heated at 160-170° for two hours till there was no more evolution of water vapour. Care was taken not to allow any drops of water to drop back into the fusion mixture. On cooling it was washed

with hot dilute alkaline solution and water and finally extracted with alcohol to remove soluble impurities. The residue crystallised from excess of boiling xylene in colourless crystalline aggregates. *Benziminazole-2-benzyl-o-phenylene diamine* (V) melts above 300°. It dissolves in acids yielding a blue solution, from which by neutralisation the original compound can be obtained. It is not hydrolysed by acids. (Found: C, 76·28; H, 6·35; N, 17·45. $C_{20}H_{18}N_4$ requires C, 76·43; H, 6·29 ; N, 17·87 per cent.).

Condensation of Phthalide with o-Phenylene diamine in absolute Alcohol by Boiling.—Phthalide (2·7 g.) and *o*-phenylene diamine (4·3 g.) were dissolved in 50 c.c. of absolute alcohol and refluxed for three hours on a water-bath. On cooling very fine colourless crystalline plates were deposited. These were recrystallised from the same solvent; *o-aminophenylaminomethyl-o'-aminobenzanilide* (VI) gave a m.p. 162°. This compound responded to the tests for primary amines. (Found: C, 72·09; H, 6·13; N, 16·62. $C_{20}H_{20}ON_4$ requires C, 72·29; H, 6·02; N, 16·87 per cent.).

The *acetyl* derivative was prepared by dissolving the compound in glacial acetic acid, adding acetyl chloride drop by drop to the mixture, and finally refluxing it for an hour. The precipitate that came down was crystallised from dilute alcohol in colourless needles, m.p. 135-136°. (Found: N, 13·21. $C_{24}H_{24}O_3N_4$ requires N, 13·46 per cent.).

Fusion of the Compound (VI).—This compound (1 g.) was heated in a test tube at 180-185° for two hours. On cooling it it was extracted with alcohol and the residue crystallised from excess of xylene in colourless crystalline aggregates. This compound had the same properties as those possessed by *benziminazole-2-benzyl-o-phenylene diamine* (V), m. p. above 300°. (Found: N, 17·47. $C_{20}H_{18}N_4$ requires N, 17·87 per cent.).

Condensation of o-Phenylene diamine with o-Oxymethylbenzoic Acid in the Presence of 4N-HCl.—*o*-Oxymethylbenzoic acid (9 g.), *o*-phenylene diamine (6 g.) and 100 c.c. of 4*N*-HCl solution were mixed and shaken well for half an hour and finally boiled under reflux for an hour. On cooling a crystalline mass deposited which was filtered and crystallised from hot water. This compound was identified to be phthalide, m. p. 73° (yield, 6 g.). The filtrate was treated with 50 per cent. sodium hydroxide solution till it was alkaline. The precipitate which came down was a mixture of *o*-phenylene diamine and *benziminazole-2-benzyl-o-phenylene diamine* (V).

The latter compound m.p. above 300° was isolated, crystallised and analysed. (Found: N, 17·46. $C_{20}H_{18}N_4$ requires N, 17·87 per cent.). The filtrate was neutralised with dilute hydrochloric acid till it was acid to congo-red. The precipitate was a mixture of phthalide and *benziminazole-2-oxymethylbenzene* (IV). This crude product was extracted with benzene and the residue crystallised from dilute alcohol in colourless plates, m. p. 237-239°. The yield was very poor. (Found: N, 12·7. $C_{12}H_{12}ON_2$ requires N, 12·5 per cent.).

Condensation of o-Phenylene diamine with o-Oxymethylbenzoic Acid in cold absolute Alcohol.—o-Oxymethylbenzoic acid (7·6 g.) was dissolved in the minimum quantity of absolute alcohol and mixed with a solution of *o*-phenylene diamine (5·4 g.). This mixture was kept overnight in a stoppered bottle upon a shaking machine at the room temperature. The next day the whole of it had precipitated as a flocculent mass. It was filtered and crystallised from a small quantity of absolute alcohol in colourless aggregates. On analysis they were found to be an *additive product* (VII) of the acid and the amine, m.p. 103-104°. They were very soluble in water and alcohol but insoluble in inert solvents. (Found: N, 10·90. $C_{14}H_{16}O_3N_2$ requires N, 10·76 per cent.).

This compound on boiling with absolute alcohol for three hours was converted into a compound, m.p. 150-152° of colourless crystalline nature. This was proved to be *o-oxymethyl-o'-aminobenzanilide* (VIII). (Found: N, 11·82. $C_{14}H_{14}O_2N_2$ requires N, 11·61 per cent.).

Condensation of o-Phenylene diamine with Phthalide in cold Absolute Alcohol.—Phthalide (6·7 g.) was dissolved in a small quantity of absolute alcohol. The mixture was kept in a stoppered bottle, overnight, with good shaking and filtered. The precipitate was crystallised from alcohol in colourless prisms. The *o-oxymethyl-o'-aminobenzanilide* (VIII) melted at 152°. (Found: N, 11·51. $C_{14}H_{14}O_2N_2$ requires N, 11·61 per cent.).

o-Benzylene-1:3-benziminazole (II).—*o*-Oxymethyl-*o'*-aminobenzanilide (5 g.) was heated in a hard glass test tube at 180-190° for a few minutes till there was no more frothing. On cooling it was extracted with absolute alcohol when a portion did not dissolve. This was filtered and crystallised from nitrobenzene in colourless crystals and identified to be *benziminazole-2-benzyl-o-phenylene diamine* (V), m.p. above 330°. From the alcoholic extract was obtained after crystallisation from xylene, colourless prismatic rossettes of *o-benzylene-1:3-benziminazole*, m.p. 185°. Repeated crystallisations from other

solvents did not raise the m.p. higher. This compound was also prepared by heating *o*-oxymethyl-*o'*-aminobenzanilide with acetic anhydride for half an hour. The crude product was decolourised with animal charcoal and then crystallised from xylene. It does not form a picrate or a chloroplatinate. (Found: C, 81·37; H, 5·32; N, 13·91. $C_{14}H_{10}N_2$ requires C, 81·55; H, 4·86 ; N, 13·73 per cent.).

Condensation of Phthalide with Ethylene Diamine.—Ethylene diamine (25 g.) and phthalide (6·7 g.) each dissolved in a small quantity of absolute alcohol, were mixed together and shaken well for some time. The reaction was completed in a little time and granular colourless crystals deposited. It crystallised from alcohol in colourless crystalline aggregates. The *o-oxymethyl-aminoethylbenzamide* melted at 179-180°. (Found: N, 14·54. $C_{10}H_{14}O_2N_2$ requires N, 14·7 per cent.).

Dihydroiminazole-2-oxymethylbenzene.—*o*-Oxymethylaminoethyl benzamide (5 g.) was boiled with 40 c c. of absolute alcohol for three hours, when on cooling a colourless crystalline compound was obtained, m.p. 210-211°. (Found: N, 15·72. $C_{10}H_{12}ON_2$ requires N, 15·9 per cent.).

o-Benzylenedihydroiminazole (X).—Dihydroiminazole-2-oxymethyl benzene (5 g.) was heated with a slight excess of acetic anhydride for an hour. The excess of anhydride was evaporated on a water-bath and the residue was extracted several times with ether and crystallised from alcohol in beautiful colourless short prisms, m.p. 152-153°. (Found: C, 75·83 ; H, 6·40; N, 17·51. $C_{10}H_{10}N_2$ requires C, 75·95; H, 6·35 ; N, 17·7 per cent.),

Condensation of Phthalaldehyde with o-Phenylene Diamine and the Formation of o-Benzylylphenylene Diamine.—Phthalaldehyde was prepared according to the method of Thiele and Guntner (*Annalen*, 1906, **347**, 102) with slight alterations in minor details, which gave long *colourless* needles on repeated crystallisation from petroleum ether, m.p. 58° (sharp). Thiele describes it as a yellow crystalline compound, m.p. 56°.

It was condensed with *o*-phenylene diamine according to the method of Thiele and Falk (*loc. cit.*). The product on repeated crystallisation from alcohol gave beautiful colourless rosettes, m.p. 213·5°. Thiele gives the m.p. as 210°. This compound does not give any tests for free aldehyde group. It easily forms a picrate and a platinum salt.

Oxidation of Benzylyl-o-phenylene Diamine (I).—The oxidation was carried out according to the method of Thiele and Falk (*loc. cit.*) and gave *o-benzoylene-1:3-benziminazole* (III) yellow prismatic needles, m.p. 211°. It was identified by a mixed melting point with the compound prepared according to the method of Bistrzycki (*loc. cit.*).

Oxidation of o-Benzylenebenziminazole (II).—*o*-Benzylenebenziminazole (10 g.) was dissolved in 30 c.c. of benzene and to this was added drop by drop a solution of 5 per cent. potassium permanganate with 2 per cent. sulphuric acid, until it was no longer decolourised when the oxidation was complete, the manganese dioxide was dissolved by means sulphur dioxide. The benzene solution was evaporated to dryness and the residue treated with hot water. The insoluble yellow residue was filtered and crystallised from alcohol. Yellow prismatic needles, m.p. 211°. This was identified with *o-benzoylene benziminazole* (III) obtained in the previous experiment by a mixed melting goint.

Oxidation of o-Benzylenedihydroiminazole.—The mothod of oxidation described in the previous experiment was followed ; but the percentages of $KMnO_4$ and H_2SO_4 were 3 and 1 respectively, because, otherwise total decomposition took place. The crude oxidation product melted indefinitely at 170-180°. The mixture was extracted with a dilute solution of sodium carbonate. The residue extracted with hot benzene, and finally crystallised from glacial acetic acid. Colourless prisms, m.p. 229-230°. The yield of *o*-benzoylene dihydroiminazole (XI) was very low. (Found: C, 69·54; H, 4·8; N, 16·51. $C_{10}H_8ON_2$ requires C, 69·76; H, 4·65; N, 16·2 per cent.). The other products of oxidation were too small for further examination. *o*-Benzoylenedihydroiminozole has also been obtained by condensing phthalic anhydride with ethylene diamine and the mixed melting point corresponds to 229°. The preparation of this compound among others will form the subject of a separate communication.

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Halogenation. Part IV. Bromination and Iodination of Aromatic Acids.

By P. S. Varma and P. B. Panicker.

Aromatic acids are not so easily brominated and iodinated as aromatic hydrocarbons or phenols or amines. Most of the bromo- and iodo-derivatives of the aromatic acids have been obtained either by the oxidation of the side-chain of the corresponding homologues of benzene or by the replacement of amino-groups in aromatic acid derivatives by bromine or iodine atoms through diazotisation (Richter, *Ber.*, 1871, **4**, 465; Hübner, Ohly and Phillip, *Annalen*, 1867, **143**, 247; Wroblewski, *Annalen*, 1873, **168**, 200; Graebe, *Annalen*, 1893, **276**, 56). *m*-Bromobenzoic acid alone has been obtained by direct bromination by heating benzoic acid with water and bromine for several days in a sealed tube at 100° or at 130°-160° (Hübner, Ohly and Phillip, *Annalen*, 1867, **143**, 233; Hübner, Petermann, *Annalen*, 1894, **281**, 246; Augerstein, *Annalen*, 1871, **158**, 4). It is difficult to obtain iodobenzoic acid by direct iodination (Peltzer, *Annalen*, 1865, **136**, 201; Birnbaum and Reinherz, *Ber.*, 1882, **15**, 456).

It has been possible to obtain a good yield of *m*-bromobenzoic acid by carrying on bromination in presence of a mixture of fuming nitric acid and nitrosulphonic acid. In presence of sodium nitrite and fuming sulphuric acid also *m*-bromobenzoic acid is obtained. *m*-Iodobenzoic acid is similarly obtained in good yield. With *p*-and *o*-toluic acids monobromo-, and monoiodo-derivatives have been obtained. *m*-Toluic acid is, however not brominated or iodinated by the same reagent. Anisic acid gives bromo- and iodo-derivatives whilst phthalic, *iso*phthalic and terephthalic acids are unaffected. Substituted benzoic acids, such as *p*-nitro-, *p*-chloro-, and *o*-bromobenzoic acids are also not halogenated.

Experimental.

The aromatic acid (5 g.), and iodine or bromine (5 g.) (with or or without any solvent) are heated on a water-bath under reflux. The mixture of fuming nitric acid and nitrosulphonic acid (10 c.c.), obtained by passing sulphur dioxide through the fuming nitric acid till a mixture containing about 50 per cent. of nitrosulphonic acid is obtained, then dropped from the top of the condenser tube in quantities of 1 c.c. at a time in course of half an hour. Then the

whole of the acid mixture is heated on the water-bath for a further period of four hours. The product is cooled and poured into cold water (200 c.c.). The unchanged iodine or bromine is removed by washing with a dilute solution of sodium bisulphite and the solid thus separated is then filtered at the pump, washed thoroughly with cold water and then recrystallised from dilute acetic acid. The product thus obtained is found to melt sharply.

When sodium nitrite and fuming sulphuric acid are used in place of the nitrosulphonic acid mixture, the sodium nitrite is placed in the flask along with benzoic acid and bromine or iodine and the fuming sulphuric acid dropped through the condenser tube. The product is then worked up exactly as before. In the experiments in which bromine is used, the unchanged bromine is removed by heating the reaction product on a water-bath in a fume cupboard. The results obtained with different substances are summarised below.

TABLE I.

Substance.	Halogen.	Solvent.	Halogenating agent.	Product and yield.
Benzoic acid (5 g.)	Iodine (5 g.)	Carbon tetrachloride (10 c.c.)	Nitrosulphonic acid mixture (10 c.c.).	*m*-Iodobenzoic acid (5·7 g.; m.p 186°).
,,	,,	,,	$NaNO_2$ (10 g.) and fuming H_2SO_4 (10 c.c.)	*m*-Iodobenzoic acid (5·2 g.; m. p. 186°).
,,	,,	No solvent	,,	*Nil.*
,,	,,	Carbon tetrachloride (10 c.c.)	Fuming HNO_3	*m*-Iodobenzoic acid (2·5 g.; m.p. 186°)
,,	,,	,,	Fuming H_2SO_4	*Nil.*
Calcium benzoate (5 g.)	,,	,,	$NaNO_2$ (10 g.) and fuming H_2SO_4 (10 c.c.).	*m*-Iodobenzoic acid (2·0 g.; m.p. 186°).
Benzoic acid (5 g.)	Bromine (5 g.)	,,	$NaNO_2$ (10 g.) and fuming H_2SO_4 (10 c.c.).	*m*-Bromobenzoic acid (4 g. m.p. 155°).
,,	,,	,,	Nitrosulphonic acid mixture (10 c.c.).	*m*-Bromobenzoic acid (6·8 g. ;m.p. 155°)
,,	,,	No solvent.	$NaNO_2$ (10 g.) and fuming H_2SO_4 (10 c.c.).	*m*-Bromobenzoic acid (2·5 g.; m.p. 155°).
p-Toluic acid (5 g.)	,,	Carbon tetrachloride (10 c.c.)	,,	3-Bromo-4-methyl benzoic acid(3·0 g.; m.p. 204°).
,,	Iodine (5 g.)	,,	,,	3-Iodo-4-methylbenzoic acid (3·0 g.; m.p. 206°).
o-Toluic acid (5 g.)	,,	,,	,,	5-Iodo-2 methylbenzoic acid (1·7 g.; m.p. 178°).
,,	Bromine (5 g.)	,,	,,	5-Bromo-2 methylbenzoic acid (2·5 g.; m.p. 167°).
Anisic acid (5 g.)	,,	Glacial acetic acid	,,	3-Bromoanisic acid (3·0 g.; m.p. 215°).
,,	Iodine (5 g.)	,,	,,	3-Iodoanisic acid (2·5 g.; m.p. 192°).

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Fluorescence in Organic Compounds.

By Sikhibhushan Dutt.

Fluorescence in organic compounds has always been attributed to a fundamental property of the molecules themselves. But an interesting phenomenon has been observed by the present author, namely, that many of the fluorescent substances when subjected to an elaborate and exhaustive process of purification, temporarily or permanently lose their fluorescence. The following eight such compounds have up to this time been prepared in a non-fluorescent condition: quinine, resacetophenone, anthracene, methylacridine, eosine, fluorescein, anthranilic acid and dicyanoquinol. In the case of fluorescein, the fluorescence does not disappear altogether but is diminished to a very considerable extent, while in other cases the disappearance is complete. It is interesting to note that most of the compounds regain their fluorescence on being kept exposed to the vitiated atmosphere of the laboratory for some time, especially on heating them to the melting point of the respective substances. The following table will summarise the results obtained during the last seven years.

Name of substance.*	No. of times crystallised.	Total time required in the process.	Yield.	Change in m.p.	Period of non-fluorescent stage.
Quinine ...	21	3 months	1·2%	2°	25-30 days.
Resacetophenone...	18	5 days	2·9	2°	3½-4 months.
Anthracene ...	22	4 months	2·6	2°	6-7 days.
Methylacridine ...	22	6 months	0·7	5°	50-60 days.
Eosine ...	35	14 months	0·2	—	1½-2 years.
Fluorescein ...	58	3½ years	0·03	—	2½-3 years.
Anthranilic acid ...	18	2 months	1·2	1°	Indefinite.
Dicyanoquinol ...	38	14 months	1·1	9°	Indefinite.

* The substances after purification were analysed ; the analytical data agreed with the theoretical values.

Although only eight compounds could be purified to a condition of non-fluorescence during seven years, yet further attempts are being made to add to the list so that they may not prove themselves rather the exception than the rule. The data that have yet been obtained are too insufficient to arrive at any generalisation of the problem.

Experimental.

Quinine.—50 G. of pure quinine nitrate in 1% solution in water were maintained at 45° in a thermostat for 144 hours while a slow stream of carbon dioxide was passed through the solution. The free base was then precipitated by ammonia and crystallised from dilute alcohol with the addition of activated charcoal and kaolin, 21 times. Finally the base was obtained in a condition in which it did not show any visible fluorescence in alcoholic or acid solution; m.p. 176°. The fluorescence gradually reappears on allowing the substance to remain exposed to the air for some days.

Resacetophenone.—It was crystallised from hot dilute hydrochloric acid (5%) 18 times with the addition of activated charcoal, when finally it was obtained in the form of colourless glistening prisms melting at 142°. These dissolved in alcohol to a colourless, and in dilute sodium hydroxide to a pale yellow solution, which are entirely devoid of any fluorescence. On allowing the substance to remain exposed to the air it gradually turns pink in colour and the fluorescence also gradually reverts. The process is very much hastened by heating the substance to the melting point.

Anthracene.—Merck's pure resublimed anthracene (150 g.) was heated in an autoclave with water (250 c.c.) at 220° for about 12 hours. The substance was then taken out, boiled with dilute sodium hydroxide solution, filtered, washed with dilute hydrochloric acid and water and finally sublimed and resublimed in steam at 180-190°, 12 times. Finally it was crystallised 10 times from glacial acetic acid containing traces of sulphur dioxide and obtained in snow white flakes melting at 215°, and entirely devoid of any blue fluorescence. The fluorescence however reappears *very quickly* in this substance specially on exposure to the vitiated atmosphere of the laboratory or by treatment with mild oxidising agents, such as, dilute nitric acid, hydrogen peroxide, potassium persulphate and so on. It also reappears on heating the substance near its melting point for a short time.

Methylacridine.—140 G. of 9-methylacridine were dissolved in dilute sulphuric acid and the solution treated with dilute barium chloride solution until barium sulphate was no longer precipitated. The resultant precipitate carried down with it much of colouring matter of the solution. The filtered solution was then treated with dilute ammonia when the methylacridine was reprecipitated. This was again dissolved in dilute sulphuric acid and the above process was repeated 9 times. The methylacridine was then dissolved in 70% alcohol and refluxed on the water-bath with kaolin and activated charcoal for about three hours. The filtered solution on dilution with cold water formed a milky emulsion which was dissolved on passing a current of sulphur dioxide through the solution. Finally on addition of dilute ammonia, the methylacridine was precipitated in fine pale yellow glistening prisms which were filtered off and recrystallised 13 times from dilute alcohol containing traces of stannous chloride. It was thus obtained in colourless prisms with silky lustre which on drying in an atmosphere of hydrogen melted at 118°, and were entirely devoid of any fluorescence. The substance was very liable to regain its blue fluorescence by oxidation in air or by treatment with any chemical oxidising agent whereby it also loses its colourlessness and assumes a pale yellow tint. The blue fluorescence also at once reappears on subliming the substance under ordinary conditions.

Eosin.—The purest available sample of Merck's eosin was dissolved in water and the free acid precipitated by the addition of dilute hydrochloric acid. This was then crystallised alternately from alcohol and acetic acid 35 times with the addition of small quantities of active charcoal. The sample of tetrabromoresorcinolphthalein thus obtained was then converted into the ammonium salt by passing a slow stream of dry ammonia over it contained in a tube, mixed with pure hydrogen. The eosin was thus obtained in glistening prisms with steel-blue metallic reflex, which dissolved in water with a beautiful pink colour entirely devoid of any fluorescence. The fluorescence however reappears in the solution by keeping it exposed to the air for two days or by passing a current of air through it. The dry solid substance however can be preserved indefinitely without regaining fluorescence, if it is kept in an air-tight vessel in the dark.

Fluorescein.—The eosin as prepared in the above instance was then reduced in 80% alcoholic solution with pure zinc and hydrochloric acid. The reduction was complete when a sample of the

substance on precipitation from alcoholic solution with water was found to be free from bromine. The fluorescein thus obtained. after 10 crystallisations from alcohol, was converted into fluorescein by oxidation in 90% acetic acid solution with the calculated quantity of freshly precipitated manganese dioxide (prepared by quantitative precipitation of pure potassium permanganate in aqueous solution with alcohol). The solution was filtered and the fluorescein precipitated from it by the addition of a saturated solution of sodium acetate. It was then filtered, washed, dried and dissolved in absolute alcohol and precipitated by petroleum ether and the last process repeated 12 times. The fluorescein was thus obtained as an orange crystalline powder which dissolved in dilute alkalis with a very pale greenish-yellow fluorescence. As a matter of fact the intensity of fluorescence was found to be reduced by nearly 95%. It could not however be obtained in a condition entirely devoid of any fluorescence. The full intensity of fluorescence reappears when the substance is heated at 200° for ten minutes, or when through the alkaline solution a current of air is passed for about 12 hours. The dry substance can however be preserved indefinitely without regaining the original fluorescence if kept in an air-tight vessel in the dark.

Anthranilic Acid.—Lead salt of the acid was prepared in the usual manner and decomposed in alcoholic suspension with hydrogen sulphide. The precipitated lead sulphide was filtered off and from the filtrate the acid was regenerated by the addition of water. This process was repeated 17 times. Finally the acid was crystallised from hot water with addition of activated charcoal 12 times, when it was obtained in colourless leaflets which dissolved in acids, alkalis or organic solvents without a trace of fluorescence; m.p. 145°. The substance does not regain fluorescence unless it is kept at the melting point for half an hour.

Dicyanoquinol.—This was crystallised from hot water containing traces of sulphurous acid and also with the addition of small quantities of activated charcoal 38 times. Thus obtained it was entirely devoid of any fluorescence. Colourless silky needles, melting at 239° with decomposition. The substance does not regain fluorescence under any condition.

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Studies on Rhythmic Formations.

By D. N. Ghosh.

Though rhythmic structures are usually produced in a suitable gel medium, the presence of a gel, however, is not indispensable. Numerous instances of rhythmic precipitations in the complete absence of a gel are known, as in the experiments of Runge ("Der Bildungstrieb der Stoffe," Oranienburg), Lenk and Brach (*Kolloid Z.*, 1911, **8**, 325), Morse and Pierce (*Z. physikal. Chem.*, 1903, **45**, 589), Dreaper (*Kolloid Z.*, 1914, **14**, 163) and Holmes (*J. Amer. Chem. Soc.*, 1918, **40**, 1187).

A remarkably well formed rhythmic precipitation of lead iodide, in the absence of any gel medium was obtained by Notboom (*Kolloid Z.*, 1923, **32**, 247). A drop of a dilute solution of potassium iodide was placed on a glass plate, which was then covered with a microscope cover slip. On putting a drop of concentrated solution of lead nitrate round the edges of the cover slip, the precipitated lead iodide began to form in well separated layers. Similar periodic structures of silver chloride between two glass plates were also obtained by Brodersen (*Kolloid Z.*, 1924, **35**, 21).

The fact that Liesegang structures can be grown in the total absence of any gel medium has actually been advanced by Notboom as a strong argument in favour of the Ostwald's supersaturation theory. In the following pages the formation of periodic precipitates in the complete absence of a gel has been studied in detail and it has been found that Notboom's conclusions in interpreting his experimental results in support of Ostwald's theory are not justified.

Experimental.

Two drops of reacting solutions were placed on a clean glass plate, and were separated from one another by a fine paraffin line. The drops were then covered with a similar glass plate, and the two advancing surfaces were just caused to meet by a slight movement of the top plate. At the junction of the two surfaces the precipitate began to form. The growth of the precipitate was followed by means

of a microscope which was fitted with a movable stage. A large number of precipitates were studied and in nearly every case distinctly periodic structures were obtained. Periodic precipitation was obtained with the following substances:—silver chromate, silver chloride, silver iodide, silver silicate, lead iodide, lead chromate, lead sulphide, barium carbonate, barium sulphate, barium oxalate, mercuric iodide, mercurous chloride, cadmium sulphide, manganese dioxide, ferric hydroxide, copper ferrocyanide and Prussian blue. In most of the above experiments a normal solution of one of the reacting substances was used against an $N/10$—solution of the other. A few of the typical structures are shown in the accompanying microphotographs.

Discussion of Results.

Periodic precipitates between two glass plates have been obtained previously with only two substances, *viz.*, with lead iodide and silver chloride. In the present paper periodic precipitates have been obtained with about sixteen different substances which show clearly that the phenomenon is quite a general one. The precipitates obtained with the sulphides showed the characteristic property of Liesegang structure, namely the distance between the precipitate layers increased with increasing distance from the centre of diffusion as can be seen from the microphotograph of the lead sulphide structure.

The experiments of Hatschek and co-workers (*Kolloid Z.*, 1912, **10**, 124), in which they were able to obtain rings of lead iodide in an agar gel already containing fine particles of lead iodide, have thrown the supersaturation theory in great doubt. It has however, been argued by Notboom that the experiments of Hatschek are inconclusive and do not disprove the supersaturation theory of Ostwald. In Hatschek's experiments the solid particles of lead iodide previously added to the gel, do not necessarily act as nuclei for releasing supersaturation as the particles have already undergone a process of adsorption, and are thus covered with a layer of the substance of the gel. In effect, the added particles of lead iodide act only as so many tiny masses of the gel and consequently possess no power of releasing supersaturation. So far as the author is aware, the above arguments of Notboom have not been satisfactorily met either by Hatschek or by any subsequent worker on the subject.

In a series of experiments the author has been able to obtain periodic precipitates of lead iodide, silver chromate and silver iodide in the presence of solid particles of the substances respectively and in the complete absence of any gel medium. Freshly precipitated lead iodide, silver chromate and silver iodide were carefully washed free from electrolytes, dried in a steam oven and finely powdered in an agate mortar. Drops of the reacting solutions were initially mixed with the finely powdered particles, placed on a glass plate separated by a fine paraffin line and were finally covered with a similar glass plate. In spite of the presence of the solid particles to act as nuclei, periodic precipitates of lead iodide, silver chromate and silver iodide were produced. Evidently then the periodic structures can be produced in the presence of solid particles uniformly distributed and in the complete absence of a gel. Notboom's arguments against the experiments of Hatschek are not applicable to the present experiments, as no gel medium, which could cover the surface of the particles by adsorption, is present. One is thus forced to the conclusion that supersaturation does not lie at the basis of any satisfactory explanation of the Liesegang phenomenon.

Brodersen (*loc. cit.*) made an ultramicroscopic examination of the precipitate formed between two glass surfaces during the course of its formation. He found that the precipitate at one stage was fine enough to show distinct Brownian movement. Notboom, however, failed to record any such movement. I have repeated the experiments of Brodersen with a large number of precipitates including lead iodide and have found that in every case the precipitate at the early stages of its formation appears as tiny particles which show very marked Brownian movements.

The experiments of Dreaper (*loc. cit.*) and of Brodersen (*loc. cit.*) show that the dimensions of the capillary spaces exert a great influence on the nature of the structures formed. This is so because on its magnitude depends the rate at which the two reacting solutions diffuse into one another. Another important factor affecting diffusion is the concentration of the reagents and in all experiments on ring-formations the use of a concentrated solution of one reagent with a weak solution of the other is well-known. It thus seems that ionic diffusion is mainly responsible for the phenomenon and accordingly the following tentative explanation for the formation of periodic precipitates in the absence of a gel is suggested.

Let us consider the case of a normal solution of lead nitrate diffusing into the thin film of an $N/10$—solution of potassium iodide enclosed between two glass plates. As soon as the two films meet, a line of precipitates is formed and if now we confine ourselves to a small section of the potassium iodide film immediately on the border line of this precipitate, we find that the depletion of iodide ions in this region, in any time t, is due to—

(*i*) Natural diffusion of iodide ions towards the lead iodide precipitate layer which is of zero iodide ion concentration;

(*ii*) Removal as lead iodide by the fast arriving lead ions. The supply of iodide ions on the other hand is due to the diffusion of the $N/10$-potassium iodide against a concentration of potassium iodide which is gradually falling from $N/10$ downwards.

It is thus apparent that this section is being impoverished of iodide ions much faster than the supply and one may therefore reasonably assume that when t is small the contration of iodide ions in this region falls so low as not to form any precipitate with the fast approaching diffusion wave of lead nitrate, which sweeps over this region leaving a gap and forms another layer of precipitate a little ahead. This process repeats itself and thus we get finally a series of stratified rings or layers.

The effect of using a weaker solution of potassium iodide will be to diminish the supply of iodide ions still more with the result that the region depleted of iodine ions will be wider. It has actually been observed that the gaps obtained with $N/100$-potassium iodide are much wide than the ones with $N/10$-potassium iodide solution. This also explains the gradual widening of the gaps towards the end in a typical Liesegang structure of lead iodide as the concentration of potassium iodide continuously falls.

In conclusion I wish to express my best thanks to Dr. P. B. Ganguly, D. Sc., for his kind interest in this work.

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Ag_2CrO_4 in presence of particles.

Ag_2CrO_4.

PbS.

AgI.

Ag_2SiO_3.

MnO_2.

Studies on the Effect of Ultra-violet Light on Colloids. Part II.

By Panna Lal and P. B. Ganguly.

In a previous paper (*J. Indian Chem. Soc.*, 1929, **6**, 547) the effect of ultra-violet light on a number of colloidal solutions has been studied, and it was found that in a majority of cases coagulation resulted. It has been shown that the coagulation of colloids by ultra-violet radiations can be satisfactorily explained on the basis of slow chemical and photochemical changes brought about by light. In the present paper a number of other colloidal solutions have been studied.

Experimental.

A series of both positively and negatively charged colloidal solutions of silver salts were prepared by Lottermoser's process (*J. pr. Chem.*, 1905, *ii*, **72**, 39). The sols were divided into two parts, one kept in the dark and the other exposed to ultra-violet light. All the sols on exposure were coagulated. The colloidal solutions kept in the dark were filtered through an ultra-filter, and the hydrogen-ion concentration of the clear filtrate was determined (*vide* Table I). The following sols were studied.

Silver Iodide Sol.

2 C.c. of 0·1*N*-silver nitrate were added drop by drop, with constant stirring to 100 c.c. of 0·003*N*-potassium iodide, whereby a clear yellowish sol was obtained. The sol was *negatively* charged and contained 0·0235 g. of silver iodide per c.c.

A positively charged silver iodide sol was also prepared by adding gradually 2 c.c. of 0·1*N*-potassium iodide to 100 c.c. of 0·003*N*-silver nitrate. The resulting *positively* charged sol also contained 0·0235 g. of silver iodide per c.c. Both the positively and negatively charged sols were coagulated on exposure to ultra-violet light, and the p_H values of the filtrates were determined (Table I).

TABLE I.

Sol.	p_H (unexposed).	p_H (exposed).
Positive silver iodide	6·78	4·50
Negative silver iodide	6·33	6·80
Positive silver arsenate	6·45	6·00
Positive silver thiocyanate	5·74	5·10
Silver (by tannin)	6·90	9·48
Silver (Carey Lea)	5·90	5·60
Vanadium pentoxide	5·28	7·12
Arsenic sulphide (negative)	4·46	3·23
Arsenic sulphide (positive)	5·26	2·32

Silver Arsenate and Silver Thiocyanate Sols.

Positively charged sols of the above substances were prepared by Lottermoser's process (*loc. cit.*). All the sols were of approximately the same concentration and contained 1·08 g. silver per 100 c.c. (Table I).

Metallic Sols.

A colloidal solution of gold was prepared by reducing 20 c.c. of boiling 0·001% solution of gold chloride by the addition of a few drops of 1% solution of tannic acid. A deep red coloured sol was obtained. A colloidal solution of silver was prepared by adding a few drops of a 1% tannic acid solution and 10% potassium carbonate solution to 100 c.c. of a 0·001*N*-silver nitrate solution. On warming, a deep reddish-brown sol was obtained. A Carey Lea's silver sol was also prepared by reducing a silver nitrate solution by a mixture of ferrous sulphate and sodium citrate. The sol was purified by repeated precipitation with ammonium nitrate and was finally stabilised by washing. On exposure to ultra-violet light the gold was practically unaffected. Both the silver sols, however, were easily coagulated (Table I).

Hydroxide Sols.

A colloidal solution of vanadium pentoxide was prepared by triturating solid ammonium vanadate with dilute hydrochloric acid and subsequent washing (Biltz, *Ber.*, 1904, **37**, 1098). A deep red sol was obtained which, however, could not be dialysed as it tended

to precipitate on dialysis. A colloidal solution of molybdenum blue was obtained by reducing an acidified solution of ammonium molybdate with sulphuretted hydrogen. The sol was dialysed till free from electrolytes. On exposure, the vanadium pentoxide sol set to a dense gel having a bright silky appearance. The molybdenum blue sol was found difficult to coagulate (Table I).

Arsenic Sulphide Sols.

To 100 c.c. of a 0·25% solution of arsenious acid 0·5 c.c. of 1% thorium nitrate solution was added and a slow stream of sulphuretted hydrogen was passed whereby a positively charged arsenic sulphide sol was obtained. A negatively charged sol of arsenic sulphide of the same cancentration was prepared from a 0·25% solution of arsenious acid. The two oppositely charged sols were exposed side by side. Both the sols coagulated but the rate of coagulation of the two oppositely charged sols was not the same: the negatively charged sol coagulated first, whereas the positively charged sol coagulated after a further exposure of several hours.

Discussion of Results.

Crowther (*Phil. Mag.*, 1929, **7**, 86), who has made an extensive study of the effect of X-radiations on colloids, has come to the conclusion that only sols in which the particles are positively charged are coagulated by X-rays, whereas negatively charged sols remain invariably unaffected. The principle underlying the above generalisation by Crowther, if it be extended to the case of the action of ultra-violet radiations on hydrosols, requires that only sols with a certain sign of charge should be affected by ultra-violet radiations, whereas an oppositely charged one should remain unchanged. Experimental results, however, run quite contrary to the above rule.

Lottermoser's silver sols, which are particularly suitable for the present purpose, as the sign of the charge on the particle can be changed at will, by using an excess of either the silver salt or of the other reacting substance, have all been found to coagulate on exposure to light. Thus both positively as well as negatively charged colloidal solutions of the iodide, arsenate, and thiocyanate of silver, when exposed to radiations under identical conditions, were all precipitated at about the same rate. This shows beyond doubt that

the coagulating effect of ultra-violet light is not limited to colloids with a particular sign of charge. The same result is obtained in the case of arsenious sulphide sol. Negatively charged arsenious sulphide, as prepared by the usual method is easily coagulated by light. When the sign of the charge was reversed by thorium nitrate, the resulting positively charged arsenious sulphide sol was also coagulated on exposure to radiations. A negatively charged gold sol, prepared by reduction with tannic acid, and a negatively charged sol of molybdenum blue were practically unchanged even after considerable exposure.

In the previous paper (*loc. cit.*) we also obtained marked coagulation with positively charged cerium and thorium hydroxide sols and failed to obtain any appreciable coagulation with negatively charged silver sols prepared by Kohlschütter's method (*Z. Elektro-chem.*, 1908, **14**, 49) and with negatively charged gum mastic sol. In view of all these experimental results, any explanation of the coagulation of colloids by radiations involving neutralisation of the charge either on the colloid particles or on the ions in the diffuse double layer, seems untenable.

On the other hand, the entire question of coagulation of colloids by radiations can be satisfactorily explained on the basis of the photochemical decomposition of the stabiliser. The coagulation observed with Lottermoser's silver sols lends considerable support to the above view. From the experimental results, it is seen that positively charged sols of the iodide, arsenate, and thiocyanate of silver develop increased acidity on exposure to ultra-violet light. The stability as well the sign of the charge in the case of the above sols, is due to the presence of an excess of silver nitrate in the system, which on exposure to light undergoes a photochemical decomposition, generating traces of nitric acid. The resulting increase in the value of the hydrogen-ion concentration after exposure, is due to this free acid. On the other hand a negatively charged silver iodide sol of the same concentration, on exposure to light, became less acidic, this being due to the small amounts of potassium hydroxide produced by the photochemical decomposition of the potassium iodide (Ross, *J. Amer. Chem. Soc.*, 1906, **28**, 786), an excess of which has to be used for the preparation of the sol.

Carey Lea's silver sol gets coagulated on exposure to light. This sol showed a marked photophoresis, the sol being coagulated on the side of the quartz tube nearest to the mercury lamp, forming a dark shining mirror. Positively charged silver iodide sol prepared by

Lottermoser's method showed a simlar photophoresis, but the deposit in this case was formed on the side away from the mercury lamp. Negatively charged silver iodide sol did not show any photophoresis.

Photochemical Changes Induced in Colloid Systems.

During the course of the present investigation we have studied the cases of two colloidal solutions in detail. *viz.*, (1) the coagulation of a silver sol stabilised by tannic acid and (2) the coagulation of a colloidal solution of thorium hydroxide prepared by the dialysis of a thorium nitrate solution.

Thorium Hydroxide Sol.

In the previous paper it was found that the p_H value of a thorium hydroxide sol increased on exposure to ultra-violet light. It was suggested that the above change in the p_H value was due mainly to the photochemical decomposition of nitric acid, which is the stabilising agent for this hydroxide sol.

To verify the above view experimentally, an approximately $N/500$-solution of nitric acid was exposed in a quartz tube to a mercury vapour lamp. The same solution was taken in another quartz tube into which a piece of platinised platinum foil ($5'' \times 1''$) was introduced and the whole system was exposed to ultra-violet light. The platinised platinum foil was carefully purified from any adsorbed electrolytes by repeated washing with and electrolysis in distilled water. The p_H values of both the exposed nitric acid solutions were compared with that of the same nitric acid solution kept in the dark. The p_H values were measured with a quinhydrone electrode, which has been found quite suitable for measuring the hydrogen-ion concentration of nitric acid solutions (Biilmann, *Trans. Faraday Soc.*, 1924, **19**, 676). The following readings were obtained:—

Nitric acid (unexposed)	p_H 2·92
Nitric acid (exposed)	3·00
Nitric acid (exposed with platinum)	3·19

Though the photochemical decomposition of moderately concentrated aqueous nitric acid is well known, very dilute solutions of nitric acid are not easily acted upon by light (Berthelot, *Compt. rend.*, 1898, **127**, 143).

The changes in the p_H value obtaind in the above experiments show, however, that in the presence of a catalytic surface, the photochemical decomposition of even dilute solutions of nitric acid is quite appreciable. It seems reasonable to infer that during the coagulation of a thorium hydroxide sol by light, the colloidal particles of thorium hydroxide exert a similar effect by offering a large catalytic surface and thus considerably promoting the photochemical decomposition of the stabiliser. In this connection certain experiments of Moore and Webster (*Proc. Roy. Soc.*, 1913, B **87**, 163; *ibid*, 1918, B **90**, 168) are interesting. They found that in the absence of certain colloids, like colloidal uranium and ferric hydroxide which act as catalysts for the photochemical synthesis of formaldehyde from carbon dioxide, the reaction either does not go or is too slow to be perceptible.

Silver Sol.

The silver sol prepared by the reduction of a dilute silver nitrate solution by a solution of tannic acid became distinctly alkaline after exposure to ultra-violet light. The stabilising agent in this case is tannic acid; consequently, if the chemical viewpoint be correct, the coagulation in this case must be due to a photochemical decomposition of the tannic acid. To test this experimentally, we have studied the effect of ultra-violet light on tannic acid solutions. An approximately 1% solution of tannic acid was exposed in a quartz tube; to another portion of the same solution a small crystal of potassium nitrate was added, and the resulting solution exposed to ultra-violet light. After an exposure of 24 hours the p_H values of the two exposed solutions were determined and the following data were obtained.

Solution.	p_H.
Tannic acid solution (unexposed)	5·58
Tannic acid solution (exposed)	3·56
Tannic acid and potassium nitrate (unexposed) ...	3·56
Tannic acid and potassium nitrate (exposed) ...	4·60

From the above results it is clear that an aqueous solution of tannic acid by itself is not appreciably decomposed, whereas in the presence of traces of potassium nitrate a considerable decomposition of the tannic acid solution sets in. During the preparation of the above silver sol, a small amount of potassium nitrate is formed (as a result of the addition of potassium carbonate) which induces photochemical changes in the tannic acid solution. This view is supported

by the fact that both in the case of the colloidal silver and in that of a solution of tannic acid containing traces of potassium nitrate, the hydrogen-ion concentrations decrease on exposure.

A further study of the reaction showed that the above decrease in acidity was due to the formation of ammonia. The amount of ammonia actually generated when a solution of tannic acid containing traces of potassium nitrate is exposed to ultra-violet light, was estimated by means of Nessler's reagent. As dilute tannic acid also reacts with Nessler's reagent, the ammonia was distilled off by passing a current of steam, and the amount of ammonia in the distillate was estimated colorimetrically by Folin's micro-Kjeldahl method. A 0·5% solution of tannic acid containing a small amount of potassium nitrate was exposed to the mercury lamp for 24 hours, and 10 c.c. of the exposed solution were treated for the estimation of ammonia. A blank experiment was also performed with a portion of the above tannic acid solution, which had been kept in the dark. 10 C.c. of the above exposed solution were found to contain 0·000125 g. of ammonia.

From the above it is clear that the coagulation of the silver sol is due to the photochemical decomposition of the tannic acid, which is the stabilising agent for this colloid. The photochemical decomposition of tannic acid is not a direct process. The small amount of potassium nitrate present in the system undergoes first a photochemical change which induces the decomposition of tannic acid by light.

Thus in the light of these experiments, the conclusion seems justified that the coagulation of a colloidal solution by light is primarily a photochemical decomposition of the stabilising ions or electrolytes. Further work is in progress.

Summary.

1. A series of colloidal solutions have been exposed to ultra-violet light, and the p_H values, of the clear filtrates obtained before and after exposure, have been measured.

2. By reversing the sign of the charge, a series of oppositely charged sols have been prepared and have been found to coagulate on exposure at about the same rate.

3. The coagulation of a thorium hydroxide sol and the observed changes in the p_H values have been found to be due to the photochemical decomposition of nitric acid, which is the stabilising agent for this sol.

4. An aqueous solution of tannic acid, containing traces of potassium nitrate, has been found to be decomposed on exposure, generating small ammounts of ammonia. The coagulation of a silver sol, stabilised by tannic acid, with the development of alkalinity, has been explained on the basis of the above experiment.

5. The experimental results obtained lend considerable support to the view that chemical and photochemical actions are responsible for the coagulation of colloids by light.

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Chemical Examination of the Seeds of *Cassia Tora*, Linn. Part I.

By H. Subba Jois and B. L. Manjunath.

Cassia tora (Chakarmarda in Sanskrit) is a shrub which thrives all over the tropical portions of India. Its leaves, seeds and roots find an important place in Ayurvedic medicine. Dymock ("Pharmacographia Indica," 1889, Vol. I, p. 516) maintains that the leaves are rich in a mucilaginous and foetid smelling material, and a decoction of these is taken internally as a gentle aperient. They are also used in the form of poultice to hasten suppuration. Fried in castor oil they are said to form a good remedy against itch and foul ulcers. The roots made into a paste with lime juice constitute a very good remedy against ring-worm. The seeds are also valuable against skin diseases. They are further used by the indigo dyers of Mysore for obtaining certain colour-effects.

A reference to the literature showed that very little work had been done on the chemical constituents of the seeds. Elborne (*Pharm. J.*, 1888-89, *iii*, **19**, 242) has reported the occurrence of a glucoside which on hydrolysis gives a substance resembling emodin. To this he ascribed the medicinal properties of the seeds. However, he has not attempted to isolate it in any quantity in order to establish definitely its chemical character. The present investigation is a more complete and systematic analysis of the seeds.

Preliminary Examination.

In order to obtain a general idea of the solubilities of the various constituents, a sample of the crushed seeds* (50 g.) was extracted successively with the following solvents, and the extracts were dried at 100°.

Petroleum ether (b. p. 40-60°)	extracted	5·2%
Ethyl ether	„	1·2
Chloroform	„	1·6
Ethyl acetate	„	2·2
Alcohol	„	6·2
Total ...		16·4%

* For the purpose of this investigation it was found necessary to have the seeds collected under close personal supervision because of the simultaneous occurrence of closely related varieties around Bangalore.

A dark brown oil was obtained from the petroleum ether extract. Ethyl ether took out a small quantity of the colouring matter occurring in the free state. The glucoside was obtained mainly in the last two extracts.

The seeds were tested with Prollius's fluid for alkaloids. The results were negative. When distilled with steam 0·003 per cent. of a pale yellow solid was obtained on extracting the distillate with pure ether. This is probably some of the colouring matter. An aqueous extract of the seeds gave tests for the presence of small amounts of reducing sugars and considerable amounts of hydrolysable polysaccharides. In this solution starch and tannin were absent. The seeds were also tested for the presence of enzymes. The powdered material (100 g.) was shaken up with sufficient water in a stoppered bottle for 48 hours. A considerable amount of carbon dioxide had been formed and the clear supernatant liquid on filtration was found to contain a large amount of reducing sugars and some soluble organic acids, presumably the products of enzyme action.

The Petroleum Ether Extract.

The Fatty Oil.—The oil from the seeds of *Cassia tora* mixed with other substances is regarded as a very useful application in several kinds of skin diseases (Dymock, *loc. cit.*, and Nadkarni, "The Indian Materia Medica," 1927, p. 185). Since no details were obtainable in the literature regarding the chemistry of this oil, it was thought interesting to submit it to detailed analysis. Owing to the low oil content, the seeds (16 kg.) were extracted by means of light petroleum (b. p. 40—60°) in a modified Soxhlet devised by Dr. M. C. T. Katti (*J. Indian Chem. Soc.*, 1930, 7, 210). After removing the solvent a dark brown pleasant smelling oil (800 g.) was obtained.

The Physical and Chemical Constants of the Oil.

Specific gravity ...	... 0·8969 at 25°
Refractive index ...	... 1·4669 at 25°
Saponification value ...	154·2
Iodine value (Hanus) ...	90·7
Acetyl value ...	9·6
Acid value	10·8
Reichert-Meisel value ...	... 0·15
Insoluble fatty acids ...	78·5%
Unsaponifiable matter ...	... 5·4%

The oil was saponified with potassium hydroxide. The resulting soap, after extraction with ether to obtain the unsaponifiable matter, was dissolved in water and acidified with hydrochloric acid when the insoluble fatty acids were liberated. These were separated into the saturated and unsaturated components by Twitchell's method (*Ind. Eng. Chem.*, 1921, **13**, 806).

Chemical Constants of the Fatty Acids.

Mean mol. wt. of mixed acids	285·7
Iodine value (Hanus)	105·2
Saturated acids (Twitchell's method)	27·2
Unsaturated acids ,, ...	72·9
Mean mol. wt. of saturated acids	272·0
,, ,, unsaturated acids	297·0
Iodine value (Hanus) of saturated acids ...	2·5
,, ,, ,, unsaturated ,, ...	142·0

The Unsaturated Acids.—The mixed unsaturated acids were found to be highly coloured. In an attempt to remove the colouring matter they were converted into their methyl esters which were distilled under reduced pressure (1 mm.). The esters passed over between 176° and 182° as a pale brown oil*. A portion of the acids liberated from this was brominated according to the method of Eibner and Muggenthaler (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", 6th edition, Vol. I, p. 585). No ether-insoluble additive compound was formed indicating the absence of linolinic acid. Among the products of bromination tetrabromostearic acid (m. p. 113-114°) was isolated. Another portion of the mixed acids dissolved in the requisite amount of weak caustic soda solution was oxidised by dilute permanganate. The crude mixture of the hydroxy acids thus obtained was extracted in a Soxhlet, first with petroleum ether to remove unoxidised acids and decomposition products, and then with ether. From this extract, after removing ether and crystallising the residue twice from alcohol, dihydroxystearic acid was obtained (m. p. 113-114°; mol. wt. 313). The re-

(*) The esters were first obtained in five different fractions whose iodine value (Hanus) gradually increased from 117·6 to 141·5. It is interesting to note that the mean mol. wt. of the acids in the different fractions was between 271 and 273. This apparent lowering is probably due to a change in the nature of colouring matter resulting in interference with the titration.

sidue in the Soxhlet after repeated crystallisations from alcohol gave pure tetrahydroxystearic acid (m. p. 158°; mol. wt. 346. Compare Katti and Puntambaker, *J. Indian Chem. Soc.*, 1930, 7, 223). As a result of these experiments the occurrence of oleic and linolic acids in the unsaturated acids has been established.

The Saturated Acids.—The mixed acids were only coloured slightly and in order to effect separation into their constituents they were converted into their methyl esters and the mixed esters (125 g.) were carefully fractionated under diminished pressure (1 mm.).

Fraction.	Range of temperature.	Distillate.	Mean mol. wt. of acids from the saponification value.
I	Up to 147°	2·4 g.	262·9
II	147°–150°	6·9	259·2
III	150°–152°	9·1	257·7
IV	153°–156°	23·9	256·8
V	156°–158°	33·8	259·5
VI	158°–162°	3·0	267·1
VII	*165°‡–168°	12·6	268·7
VIII	168°–171°	12·7	278·0
IX	171°–186°	1·1	283·2
X	186°–188°	4·9	298·4
XI	188°–210°	6·3	327·4
XII	Residue including loss	8·3	368·0 (of the purified acid).

Fractions I—V.—From each of these fractions pure palmitic acid (m. p. 62·5°; mol. wt. 256·1) was isolated as the principal constituent. The identity of the palmitic acid obtained was further established by taking a mixed m. p. with an authentic specimen of the pure acid. The filtrates gave a fraction melting at 59—60° (mol. wt. 264).

Fractions VI—IX.—From these fractions was obtained a substance which melted at 62—63° (mol. wt. 285). Repeated recrystallisations from various solvents did not alter either its m. p. or mean mol. wt. Although the mol. wt. corresponded to that of stearic acid, the m. p. was considerably lower. When a mixed m. p. with pure stearic acid was taken considerable depresssion was observed.

Acid fraction from the filtrates of above had m. p. 57-58·5°, and mean mol. wt. 272).

* Only a few drops of the distillate passed over between 162° and 165°.

Fraction X.—The acid obtained on crystallisation from alcohol melted at 68° (mol. wt. 335·7) and it was noticed that with successive recrystallisations both the m. p. and the mol. wt. began to increase. But it was not possible to isolate any definite acid.

Fraction XI.—On repeated recrystallisations of the acid from this fraction was obtained a substance melting at 74-75° and whose mean mol. wt. was 350. This also proved to be a fraction that could not be resolved by repeated crystallisations (compare Katti and Manjunath, *J. Indian Chem. Soc.*, 1929, **6**, 843).

Fraction XII.—The residue in the distillation flask was found to be very deeply coloured. It was dissolved in alcohol, saponified and the soap was dissolved in excess of hot water. The fatty acid was precipitated by the addition of excess of dilute hydrochloric acid. This acid (2 g.) was dissolved in alcohol and refluxed with animal charcoal for a few hours. The crystallised product (m. p. 74-75°; mol. wt. 368) was then repeatedly recrystallised from various solvents including acetone and ethyl acetate. Its m. p. rose up to 76—77·5° while the mol. wt. remained the same. A mixed m. p. with pure lignoceric acid was taken and since no difference was noticed its identity was regarded as established (compare Katti and Manjunath, *loc. cit.*, p. 844).

It is interesting to note that although the mean mol. wt. of the mixed solid acids (272) correspond very nearly to that of an equimolecular mixture of palmitic and stearic acids, no trace of the latter was obtained in the above work. Again since no definite acid was found between palmitic and lignoceric acids, it was thought necessary to mix together all the higher acid fractions except the twelfth, and to fractionate their methyl esters (30 g.) very carefully under reduced pressure (1 mm.).

Fraction.	Range of temperature.	Mean mol. wt. of acids liberated from the esters and recrystallised from alcohol.	M. p. of acids in the last column.
I	152°–155°	253	62–63°
II	155°–160°	259·6	61–62°
III	160°–165°	259·8	,,
IV	165°–170°	262·0	56·5–57·5°
V	170°–175°	280·6	59–60°
VI	175°–185°	291·7	59–61°
VII	185°–200°	332·6	62–64°
VIII	200°–210°	344·7	72·5–73·5°
IX	Residue.	368·7	74–75°

Thus it was noticed that the lower fractions (I—III) consisted of palmitic acid. The acids obtained from the Fractions IV—VI with successive crystallisations gave increasing mean mol. wts. and melting points. Fraction VIII gave an acid whose mol. wt. remained constant inspite of several recrystallisations. Finally from the residue was obtained a small quantity of 'crude lignoceric acid.' It is interesting to note that acid fraction of mean mol. wt. 350 from the first fractionation (Fraction XI) could not be isolated again. This was taken as a proof that it was a mixture.

Thus from the solid acids palmitic and lignoceric acids only could be isolated.

The Unsaponifiable Matter.

An oily, reddish semi-solid was left behind after evaporating off the ether used to extract the saponified oil. From this a phytosterol (m. p. 133-134°) was obtained in a colourless and pure state after repeated treatments with animal charcoal and recrystallisations from alcohol. Its acetyl derivative melted at 120°. The red oil from mother-liquors of the phytosterol was treated with digitonine. After removing the precipitate, from the residues it was not possible to isolate any other compound.

Thus during this investigation the following compounds were found to be present in the fatty oil.

(*i*) Oleic and linolic acids among unsaturated acids.
(*ii*) Palmitic and lignoceric acids among saturated acids.
(*iii*) Sitosterol in the unsaponifiable matter.

An examination of the other constituents of the seeds of *Cassia tora* will form the subject of a later communication.

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Studies in Quinoline Compounds. Part I.

By Upendra Nath Brahmachari and Tarapada Bhattacharjee.

The object of this paper is to study a series of quinoline compounds with the view of discovering those that are likely to possess anti-protozoic and therapeutic properties.

Of the compounds described here, the first series contains a vinyl grouping. The presence of vinyl grouping in these compounds is comparable to the same group being present in quinine and allied compounds having therapeutic properties. These compounds possess certain definite properties, which are absent in the second series. They are generally yellow in colour and exhibit a blue fluorescence in dilute alcoholic solution. They are extremely insoluble in water, but dissolve fairly in alcohol, acetone and ether. They give a dark red colouration with acids. Their salts are hydrolysed in excess of water.

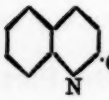
These compounds have been prepared from quinaldine and its derivatives by condensing them with *p*-dimethylaminobenzaldehyde. The reactivity of the α-methyl group in quinaldine has been taken advantage of in its condensation with this aldehyde. In the preparation of these compounds we have not taken the help of any condensing agent, as simply the heating of the reactants brings about their combination.

The second series of compounds have been obtained from the various aminoquinolines by condensing them with chloroacetamide. These compounds are not so much insoluble in water as compounds of the first series. They exhibit no fluorescence. Their salts are not hydrolysed by excess of water and they are generally colourless. Acids dissolve them without giving rise to any colour.

Experimental.

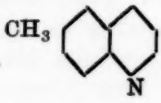
First Series.

2-p-Dimethylaminostyrylquinoline.



Quinaldine (2 g.) and *p*-dimethylaminobenzaldehyde (2 g.) are heated carefully in a dry test tube to gentle boiling for about 15 minutes over a small flame. The mixture is then dissolved in boiling alcohol and filtered. The filtrate on cooling deposits the above compound. It is then collected and dried (also *vide* Neolting and Witter, *Ber.*, 1906, **39**, 2479); m. p. 175°. (Found: N, 10·5. $C_{19}H_{18}N_2$ requires N, 10·2 per cent.).

6-Methyl-2-p-dimethylaminostyrylquinoline.



6-Methylquinaldine (1 g.) is mixed in a dry test tube with *p*-dimethylaminobenzaldehyde (1 g.) and the mixture heated carefully to gentle boiling over a small flame for about 15 minutes. The substance is purified and dried in the same way as in the previous case. It melted at 199°. (Found: N, 9·9. $C_{20}H_{20}N_2$ requires N, 9·7 per cent.).

6-Oxy-2-p-dimethylaminostyrylquinoline.

6-Oxyquinaldine (2 g.) and *p*-dimethylaminobenzaldehyde (2 g.) are mixed together and heated carefully to gentle boiling over a small flame for about 10 minutes. Acetone is then added in excess to the product. The hydroxy-derivative remains undissolved. It is separated and dried; m. p. above 240°. (Found: N, 9·89. $C_{19}H_{18}ON_2$ requires N, 9·65 per cent.).

6-Ethoxy-2-p-dimethylaminostyrylquinoline.

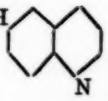
6-Ethoxyquinaldine (2 g.) and *p*-dimethylaminobenzaldehyde (2 g.) are heated carefully to gentle boiling over a small flame for 10 minutes. The product is poured into water. The solid thus separated is then purified by recrystallisation from ether; m.p.212°. (Found: N, 9·15. $C_{21}H_{22}ON_2$ requires N, 8·81 per cent.).

6-Methoxy-2-p-dimethylaminostyrylquinoline.

6-Methoxyquinaldine (2 g.) and *p*-dimethylaminobenzaldehyde (2 g.) are condensed by heating for 15 minutes. The product is then dissolved in alcohol. Water precipitates the base from the alcoholic solution. It is then extracted with ether. The ethereal solution is then dried over fused calcium chloride and the ether removed. The residual solid thus obtained is then dried in vacuum; m.p. 202°. (Found: N, 9·45. $C_{20}H_{20}ON_2$ requires N, 9·2 per cent.).

SECOND SERIES.

Quinoline-6-aminoacetamide, $NH_2 \cdot CO \cdot CH_2 \cdot NH$



6-Aminoquinoline hydrochloride (4 g.) is dissolved in 20 c.c. of water and chloroacetamide (2·5 g.) added to it. The whole is then boiled for about 3 hours. It is then filtered, and the filtrate cooled with ice and made alkaline with a saturated solution of sodium carbonate, when the required compound separates out. It is filtered, recrystallised from alcohol and dried on a porous plate; m.p. 197°. (Found: N, 21·3. $C_{11}H_{11}ON_3$ requires N, 20·9 per cent.).

Quinoline-8-aminoacetamide.

This compouud is prepared by boiling a solution of 8-aminoquinoline hydrochloride and chloroacetamide in water in equimolecular proportions for 3 hours. The condensation product is then separated by adding sodium carbonate and then purified by recrystallising from alcohol; m.p. 183°. (Found: N, 21·25. $C_{11}H_{11}ON_3$ requires N, 20·9 per cent.).

6-Ethoxyquinoline-8-aminoacetamide.

6-Ethoxy-8-aminoquinoline hydrochloride and chloroacetamide are dissolved in water in equimolecular proportions and the aqueous solution is boiled for 3 hours. The final product is isolated and purified as above; m.p. 235°. (Found: N, 16·88. $C_{13}H_{15}O_2N_3$ requires N, 17·1 per cent.).

6-Methoxyquinoline-8-aminoacetamide.

Equimolecular proportions of 6-methoxy-8-aminoquinoline hydrochloride and chloroacetamide are dissolved in water and the solution boiled for 3 hours. The product is separated and purified in the usual way; m.p. 226°. (Found: N, 17·89. $C_{12}H_{13}O_2N_3$ requires N, 18·2 per cent.).

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Fermentation of Rice Straw by *Bacillus Acetoethylicus*.

By Vinayak Narayan Patwardhan.

That pentoses could be fermented by some bacteria has long been known to bacteriologists. With *Bac. ethaceticus* Frankland (*J. Chem. Soc.*, 1892, **60**, 432, 737) obtained 11·2-12·3 per cent. of alcohol from arabinose. Tollens (*J. Inst. Brewing*, 1898, **4**, 438) experimented upon an organism which produced ethyl alcohol from xylose.

Northrop, Ashe and Senior (*J. Biol. Chem.*, 1919, **39**, 1) reported the isolation of a bacterium capable of fermenting pentoses and hexoses to acetone and ethyl alcohol. They named the organism *Bacillus acetoethylicus*. They obtained 18 to 20 per cent. alcohol with 4 to 5 per cent. of acetone calculating on the quantities of sugar fermented. Attempts to utilise *Bac. acetoethylicus* to produce alcohol and acetone from pentoses were made the subjects of study by Northrop and his collaborators (*J. Ind. Eng. Chem.*, 1919, **11**, 728), Peterson, Fred and Verhulst (*J. Ind. Eng. Chem.*, 1921, **13**, 757) and Fred, Peterson and Anderson (*J. Ind. Eng. Chem.*, 1923, **15**, 126). The general conclusion reached by the different authors is that the fermentation of pentoses by *Bac. acetoethylicus* is normally slow taking from eight to ten days for completion. Northrop, Ashe and Morgan claimed an increase in the rate of fermentation by addition of oak or beech shavings to the fermenting mixture. Peterson, Fred and Verhulst (*loc. cit.*) stated that addition of peptone and disodium phosphate and the maintenance of the reaction of the fermenting liquid between p_H 6 and 9 by suitable addition of calcium carbonate hastened the fermentation.

In addition to fermenting pentoses and hexoses to ethyl alcohol and acetone, the organism also converts a part of the sugar supplied into formic and acetic acids. Thus Fred, Peterson and Anderson obtained from hydrolysed oat hulls 26·9 per cent. of alcohol, 12·7 per cent. of acetone and 6·71 per cent. of volatile fatty acids. Donker ("Bijdrage tot de Kennis, der Boterzuur-Butylalcohol en acetonegistung," Publ. W. D. Meinema, Delft, 1926) states that from hexoses he obtained about 2·6 per cent. of formic acid and 5·2 per

cent. of acetic acid. Thaysen and Galloway (*Ann. Appl. Biol.*, 1928, **15**, 392) obtained from hydrolysed wheat straw 1·77 per cent. of acetic acid and 12·6 per cent. of formic acid. They also found that the concentration of acetone was higher when the fermenting medium contained hexoses than when only pentoses were present. According to them the yields of acetone and alcohol were always variable. Neither increase in the internal surface nor the addition of peptone and dipotassium phosphate improved the rate of conversion to any appreciable extent.

Thaysen ("Fuel for Motor Transport," Fourth Memorandum, published by His Majesty's Stationery Office, 1927) made an extensive study of the possibility of converting cellulosic waste materials into the fermentable sugars. He concluded that the best results were obtained when the grasses and straw were steeped in two per cent. sulphuric acid for four hours followed by steaming for six hours at ordinary pressure. Unpublished work done in this laboratory showed that the time of steeping did not matter so long as acid was allowed to be uniformly soaked up by the straw, for which purpose one hour was found to be sufficient.

It was found that Thaysen's figures for pentoses obtained from rice straw by his process could not be confirmed. With one hours' steeping in two per cent. sulphuric acid followed by six hour's steaming at atmospheric pressure only six to seven per cent. of reducing sugars were obtained. Similar experiments with four per cent. and six per cent. acids almost doubled and trebled the yields of reducing sugars. The straw used for this purpose was local rice straw and not the Burma variety which was used by Thaysen.

All the previous workers found that *Bac. acetoethylicus* would ferment only small concentrations of pentoses. The bacillus would not ferment 5 per cent. sugar solution, but gave satisfactory results when the concentrations ranged between 2 and 3 per cent. It was with a view to train the bacillus to ferment concentrations of pentoses higher than these that the present piece of work was undertaken.

The observation of the previous workers that the best results were obtained by keeping the concentration of pentoses near about three per cent. was confirmed.

It was observed that increasing the concentrations of sugars above three per cent. generally decreased the yields of alcohol and acetone till at 7 per cent. the yields were reduced to quantities of little practical use. Changing the nutrient mixtures from ammonium

phosphate and peptone to combinations of ammonium nitrate, disodium hydrogen phosphate and yeast water did not materially improve the yields.

When carrying out subcultures to train the organism to higher concentration of pentoses, it was observed that the presence of small quantities of hexoses, such as glucose, always facilitated the growth of the organism and the fermentation of pentoses. The bacillus was trained to ferment 7 per cent. pentoses. Starting from a concentration of three per cent. first it was acclimatised to five per cent. and then to seven per cent. pentose concentration. In this process diminishing quantities of added hexoses were used with increasing concentration of pentoses until an abundant growth of the organism and vigorous fermentation were obtained.

Experimental.

Hydrolysis of Straw by dilute Suphuric Acid.—A weighed quantity of chopped straw (100 g.) was packed into a lead pot and steeped for one hour in a definite volume of sulphuric acid of known strength. After squeezing out the superfluous sulphuric acid, the residue was steamed for six hours at atmospheric pressure. Reducing sugars were washed and pressed out from the digested straw and after neutralising with calcium carbonate were estimated as usual. Yields of reducing sugars are presented in Table I.

Table I.

Per cent. acid.	2	4	6
Per cent. reducing sugars as hexoses.	6·9-9·5	11·6	18·9

To obtain a good yield of reducing sugars a much higher percentage of acid than the one recommended by Thaysen has to be used. About 400 c. c. of dilute acid were generally required for hydrolysing 100 g. of straw.

Fermentation of the Hydrolysed Straw by Bacillus Acetoethylicus. —(*a*) Fermentations were carried out at 37° for 8—10 days in small flasks containing measured quantities of the concentrated hydrolysate together with ammonium phosphate and either peptone or yeast water. It was found that a very small concentration of peptone favoured good growth and fermentation, the optimum being about 0·05% (Table II).

TABLE II.

(Total reducing sugar before fermentation was 3·35 g.)

Peptone.	Sugar fermented.	Acetone-alcohol mixture.
0·00%	0·37 g.	0·027 g.
0·05	2·70	0·565
0·10	2·71	0·484
0·20	2·29	0·366
0·40	2·31	0·183

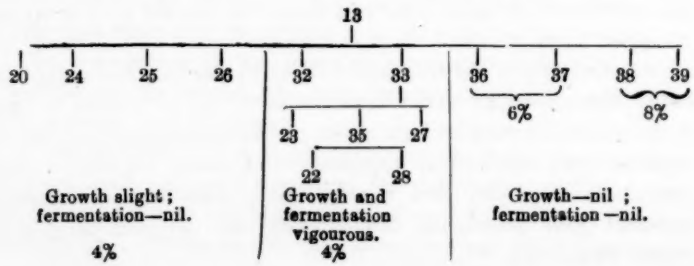
Substitution of peptone by yeast water did not improve the yields.

(*b*) *Experiment to show the necessity of hexoses in the medium for training the bacillus to ferment higher concentrations of pentoses.* It was found that *Bacillus acetoethylicus* could not be raised successfully on a medium containing exclusively high concentration of pentoses. However, when mixed with a small quantity of hexoses the inoculated bacillus grew very well on the pentose medium and fermented vigorously. After one or two such transfers it developed the capacity to ferment a pure pentose medium. The following tabulated observations will bear out the statement.

Flasks 21 to 30 both inclusive contained identical media with 4% reducing sugar. The latter was entirely pentose, all the hexoses having been fermented away by a strain of acclimatised yeast.

Flasks 32 to 35 both inclusive contained another set of identical media, the total of 4% reducing sugars being made up of approximately 75% pentoses and 25% hexoses. (Rice straw extracted with dilute sulphuric acid for half an hour at 4 to 5 atmospheres pressure yields such a mixture.

Flask no. 13 contained a vigorously fermenting mixture of 3% pentoses. This flask was used as a starting point for inoculation.



Figures indicate percentage of reducing sugars in the media. The bacillus was trained to ferment 7% pentose medium in the following steps:

Medium.	Pentose (straw extract).	Glucose added.	Transfers.
1	4·5%	0·5%	2
2	5·0	2·0	2
3	5·5	1·5	2
4	6·0	1·0	2
5	6·5	0·5	1
6	7·0	0·0	—

(*c*) The *yield of acetone-alcohol mixtures* varied considerably, no direct cause being found for this variation. The best results obtained utilising 4% reducing sugar solutions are given below in Table III.

Reducing sugar in all flasks before fermentation was 4·1 g. per 100 c. c. of reaction mixture. Flasks were incubated at 37° for seven days.

TABLE III.

Flask no.	Sugar fermented.	Acetone—alcohol mixture.
16	3·24 g.	0·6089 g.
18	3·24	0·7166
19	3·30	0·6726
23	3·36	0·6386
27	3·20	0·7424

(*d*) *Some fermentation results with media containing 7% reducing sugars.*

TABLE IV.

Flask no.	Total sugar before fermentation.	Total sugar after fermentation.	Acetone—alcohol.	Total acid: equivalent to c.c. of *N*/10-alkali.
71	3·4 g.	0·840 g.	0·404 g.	—
72	3·4	0·550	0·446	43·0
76	3·4	0·460	0·350	49·3
78	3·5	0·680	0·288	37·2
81	3·5	0·437	0·434	47·0

The results given above represent the best of the lot. The range of loss of sugars by fermentation lay between 75 and 87%. The corresponding production of acetone and alcohol mixture was considerably less than that from 4% sugar media. In other cases, where about the same percentage of sugars were lost, the power mixture was still less than what the figures represent in Table IV.

Summary.

(1) It has not been found practicable to train *Bac. acetoethylicus* to ferment high concentrations of pentoses, *e.g.*, 7 per cent. The yields of acetone—alcohol mixtures obtained from fermenting 7 per cent. pentoses (present in the straw hydrolysate) were too low to be of any practical importance from the viewpoint of commercial application.

(2) In training the bacillus for the above purpose the presence of hexoses in small quantities were found to be necessary at each step in the increase in pentose concentration.

The author has great pleasure in acknowledging useful suggestions made by Dr. V. Subrahmanyam during the course of this work.

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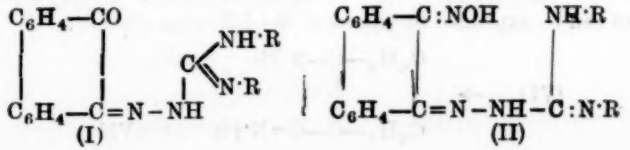
Action of Hydrazides. Part IV. Condensation of Diarylaminoguanidines with Phenanthraquinone and some of its Derivatives.

By Satish Chandra De and Devendra Nath Dutt.

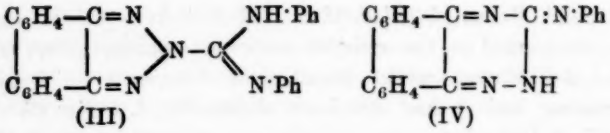
Thiele and Behan (*Annalen*, 1898, **302**, 303) have shown that osazones are formed in the reaction between aminoguanidine and aliphatic-1:2-diketones whilst benzil gives 3-amino-5:6-diphenyl-1:2:4-triazine; and it has also been shown (De, *J. Indian Chem. Soc.*, 1927, **4**, 183) that aminoguanidine reacts with most of the aromatic 1:2-diketones to yield triazines. Here the tendency to form ring compounds with the simultaneous elimination of two molecules of water has been attributed to the greater basicity of aminoguanidine which contains an amino-group in addition to a hydrazine residue.

In the present paper diphenylaminoguanidine, di-*p*-tolylaminoguanidine and di-β-naphthylaminoguanidine have been condensed with phenanthraquinone, its 2-nitro- and 2:7-dinitro-substitution products. The object of the present communication is to see what happens if the basicity of the amino-group in $-C(:NH)\cdot NH_2$ of aminiguanidine is diminished by taking the aryl substitution products mentioned before. It should be observed here that by taking the aryl substitution products of aminoguanidine, the formation of a triazine ring by immediate elimination of water from the diarylaminoguanidinephenanthraquinone (I) is prevented, and consequently the first product of the reaction will have a hydrazone structure. When the monoxime of phenanthraquinone or its substitution products are condensed with the various diarylaminoguanidines in alcoholic solution the hydrazone-oximes are formed in good yield by the elimination of a molecule of water. When the same reactions are allowed to take place in glacial acetic acid solution or when the hydrazone-oximes are heated with glacial acetic acid, different compounds are formed.



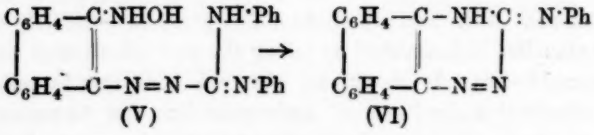
(I) (II)

As has been shown (De, *J. Indian Chem. Soc.*, 1928, **5**, 373) that when phenanthraquinonemonoxime and carbohydrazide (or thiocarbohydrazide) are allowed to react, the product obtained is a bistriazole derivative, so it might be expected by analogy that the compound derived from phenanthraquinonemonoxime and diphenyl aminoguanidine *e.g.*, should have a similar triazole structure (III) or the product might be a triazine derivative (IV).



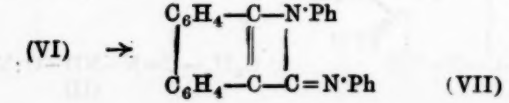
(III) (IV)

A triazine ring somewhat different from the one suggested above can also be supposed to be formed in which the elimination of a molecule of hydroxylamine is to be presumed. To account for this the migration of a hydrogen atom must first be assumed forming an intermediate azo-compound (V) which will then part with a molecule of phenylhydroxylamine to form the triazine (VI). The mechanism of the reaction can be illustrated, thus:



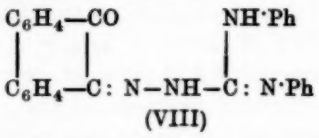
(V) (VI)

But the compound actually isolated is neither (III) nor (IV) or (VI). From the analytical results it appears that the compound from phenanthraquinonemonoxime and diphenylaminoguanidine, for example, possesses an empirical formula, $C_{27}H_{18}N_2$. The only possible way in which the formation of such a compound can be explained is that the moment the azo-compound is formed it undergoes fission at the azo-linking with the liberation of two atoms of nitrogen and the carbon atoms become linked together with the formation of an unstable compound which then parts with a molecule of hydroxylamine to form a ring (VII). The various changes can be explained by means of the following scheme:

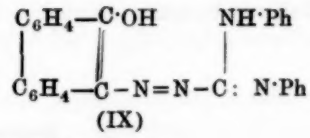


(VI) (VII)

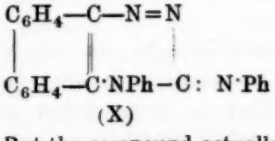
The migration of a hydrogen atom in diarylaminoguanidine phenanthraquinonemonoxime to facilitate the formation of a four-membered ring, at once suggested itself whether it was possible to obtain ring-compounds from the various diarylaminoguanidine phenanthraquinones. In all these cases if the reaction proceeds normally two compounds may possibly be formed from each of these compounds, namely, one by the elimination of a molecule of water and the other by the loss of phenylhydroxylamine. The reaction can be explained by taking, for example, diphenylaminoguanidinephenanthraquinone (VIII) which is first transformed into an intermediate azo-compound (IX) from which there results either 3-phenylimino-4-phenyl-1:2:4-phenanthrotriazine (X) or anilinophenanthrodiazole (XI).



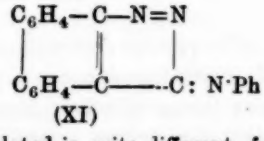
(VIII)



(IX)

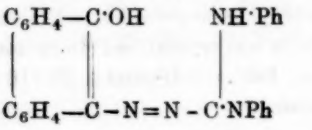


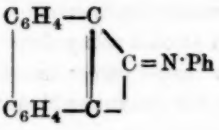
(X)



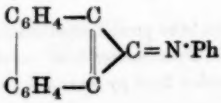
(XI)

But the compound actually isolated is quite different from (X) or (XI) as it contains a very low percentage of nitrogen than what is demanded by the compound (X) or (XI). The analytical results show that this compound should be derived from compound (XI) with two atoms of nitrogen less. The only possible way to explain the formation of such a compound is that the azo-compound (IX) momentarily formed, simultaneously parts with the group -N=N- and a molecule of phenylhydroxylamine and an unstable compound (XII) is formed with the carbon valencies free, this then uniting to form the compound (XIII), thus:





(XII(



(XIII)

Although the elimination of nitrogen from compounds of this type is not to be found in literature and appears to be the first of its kind yet such a phenomenon in ring-compounds is not altogether new (Buchner and Curtius, *Ber.*, 1885, **18**, 237; Pechmann, *Ber.*, 1898, **31**, 2950; Schlotterbeck, *Ber.*, 1907, **40**, 479; etc.). It should be marked here that in all the cyclic compounds from which nitrogen is known to be eliminated, the two nitrogen atoms are linked together by a double bond; and it appears to the present authors that in all the cases examined such a linkage between the nitrogen atoms is probably formed by the migration of a hydrogen atom as postulated, and compounds of the types (VI and XI) are actually produced which, being unstable under the experimental condition, part with nitrogen. Similar reactions have been observed in other cases which will shortly be communicated.

Experimental.

Phenanthraquinone diphenylaminoguanidine.—In an alcoholic solution of phenanthraquinone and diphenylaminoguanidine, there was a sudden change of colour from yellow to orange-yellow with the separation of a yellow crystalline product which was recrystallised from pyridine in deep yellow needles, m.p. 240°. (Found: N, 13·29. $C_{27}H_{20}ON_4$ requires N, 13·46 per cent.).

The above compound was heated in presence of acetic acid for 5 to 6 hours when the colour changed from yellow to orange and finally to green. The solution was filtered from the substance which was successively boiled with acetic acid and pyridine and crystallised from nitrobenzene in green plates, m. p. above 300°. (Found: C, 90·55; H, 4·84; N, 4·80. $C_{21}H_{13}N$ requires C, 90·32; H, 4·66 ; N, 5·02 per cent.).

Phenanthraquinonemonoxime diphenylaminoguanidine was obtained from alcohol as a yellow mass which was crystallised from acetic acid in deep yellow needles, m.p. 158°. (Found: N, 16·53. $C_{27}H_{21}ON_5$ requires N, 16·24 per cent.).

N.B.—That nitrogen is actually evolved has been proved experimentally by collecting the gas (air being first of all driven off) in a nitrometer over caustic potash and driving off the evolved nitrogen from the reaction flask by means of carbon dioxide.

The above compound was heated in acetic acid solution for 4 to 5 hours. The solid so obtained was crystallised from alcohol in yellow rectangles, m.p. 180° (decomp.). (Found: C, 87·76; H, 4·99; N, 7·70. $C_{27}H_{18}N_2$ requires C, 87·55; H, 4·86; N, 7·55 per cent.).

2-*Nitrophenanthraquinonediphenylaminoguanidine*.—From an alcoholic solution of diphenylaminoguanidine and 2-nitrophenanthraquinone separated a red product which was crystallised from pyridine in red rectangles, m.p. 238°. (Found: N, 15·37. $C_{27}H_{19}O_3N_5$ requires N, 15·18 per cent.).

The above substance when heated for 5 to 6 hours with acetic acid gradually went into solution and then a solid product separated. This was successively boiled with acetic acid and pyridine and the residue crystallised from nitrobenzene, m.p. above 300°. (Found: C, 77·98; H, 3·86; N, 8·79. $C_{21}H_{12}O_2N_2$ requires C, 77·77; H, 3·74; N, 8·64 per cent.).

2-*Nitrophenanthraquinonemonoxime diphenylaminoguanidine*—, separated from alcohol and was crystallised from a mixture of water and pyridine in red needles, m.p. 233°. (Found: N, 18·02. $C_{27}H_{20}O_3N_6$ requires N, 17·65 per cent.).

The above substance was heated with acetic acid for 5 to 6 hours and the solid that separated was crystallised from alcohol, m.p. 193°. (Found: C, 78·30; H, 4·24; N, 10·24. $C_{27}H_{17}O_2N_3$ requires C, 78·07; H, 4·09; N, 10·12 per cent.).

2:7-*Dinitrophenanthraquinone diphenylaminoguinidine* separated from alcohol as a dark coloured solid which was crystallised from a mixture of pyridine and water in violet rectangles, m.p. 235°. (Found: N, 16·84. $C_{27}H_{18}O_5N_6$ requires N, 16·60 per cent.).

The above substance was heated with acetic acid for 5 to 6 hours when the violet colour of the solid was gradually changed to green. This was then boiled with pyridine and acetic acid and the residue was crystallised from nitrobenzene as a green crystalline power, m.p. above 300°. (Found: C, 68·54; H, 3·13; N, 11·48. $C_{21}H_{11}O_4N_3$ requires C, 68·29; H, 2·99; N, 11·38 per cent.).

2:7-*Dinitrophenanthraquinonemonoxine diphenylaminoguanidine* obtained from the components in alcoholic solution when the colour of the monoxime gradually changed to green. This was crystallised from pyridine and water. The colour changes to brown at 230° and melts at 245°. (Found: N, 18·98. $C_{27}H_{19}O_5N_7$ requires N, 18·81 per cent.).

The above substance was heated with glacial acetic acid for 2 to 3 hours. The solid was crystallised from a mixture of pyridine and water, m.p. 202°. (Found: N, 12·66. $C_{27}H_{16}O_4N_4$ requires N, 12·18 per cent.).

Phenanthraquinone di-p-tolylaminoguanidine, obtained from the components and alcohol as a red solid mass was crystallised from pyridine in red rectangles, m.p. 236°. (Found: N, 12·75. $C_{29}H_{24}ON_4$ requires N, 12·61 per cent.).

The above substance was heated with acetic acid for 3 to 4 hours when the colour changed from red to brown. The solid separated, boiled with pyridine and the residue recrystallised from nitrobenzene, m.p. above 300°. (Found: C, 90·32; H, 5·01; N, 4·93. $C_{22}H_{15}N$ requires C, 90·10; H, 5·12; N, 4·77 per cent.).

Phenanthraquinonemonoxime di-p-tolylaminoguanidine, obtained by heating the components with alcohol, was crystallised from pyridine in red rectangles, m.p. 227°. (Found: N, 15·42. $C_{29}H_{25}ON_5$ requires N, 15·25 per cent.).

The above compound was heated with acetic acid from 5 to 6 hours when the red colour was changed to deep yellow. The solid was then separated and crystallised from a mixture of water and alcohol in yellow rectangles, m.p. 156°. (Found: C, 87·73; H, 5·05 N, 7·42. $C_{28}H_{20}N_2$ requires C, 87·50; H, 4·94; N, 7·29 per cent.).

2-Nitrophenanthraquinone di-p-tolylaminoguanidine, obtained from alcohol as a brown precipitate, was crystallised from pyridine in brown rectangles, m.p. 228°. (Found: N, 14·55. $C_{29}H_{23}O_3N_5$ requires N, 14·31 per cent.).

The above substance was heated in acetic acid suspension for 4 to 5 hours when the brown colour was changed to bluish-black. This was boiled with acetic acid and pyridine and the residue crystallised from nitrobenzene, m.p. above 300°. (Found: C, 78·32; H, 4·23. $C_{22}H_{14}O_2N_2$ requires C, 78·10; H, 4·08 per cent.).

2-Nitrophenanthraquinonemonoxime di-p-tolylaminoguanidine, separated from alcohol as a red mass, was crystallised from a mixture of pyridine and water in red rectangles, m.p. 228°. (Found: N, 16·82. $C_{29}H_{24}O_3N_6$ requires N, 16·66 per cent.).

The above substance was heated in acetic acid suspension for 5 to 6 hours and the separated greenish-yellow solid was boiled with pyridine and the residue crystallised from nitrobenzene in rectangles, m.p. 190°. (Found: C, 78·53; H, 4·61. $C_{28}H_{19}O_2N_3$ requires C, 78·32; H, 4·43 per cent.).

2:7-*Dinitrophenanthraquinone di-p-tolylaminoguanidine* was crystallised from pyridine, m.p. 263°. (Found: N, 15·94. $C_{29}H_{22}O_5N_6$ requires N, 15·73 per cent.).

The above compound was heated for 5 to 6 hours in acetic acid suspension. The separated yellowish-green solid was boiled with pyridine and the residue was crystallised from nitrobenzene in green plates, m.p. above 300°. (Found: C, 68·80; H, 3·53. $C_{22}H_{13}O_4N_3$ requires C, 68·93; H, 3·39 per cent.).

2:7-*Dinitrophenanthraquinonemonoxime di-p-tolylaminoguanidine* which separated from alcohol as a yellow mass could not be crystallised from any solvent, m.p. above 300°. (Found: N, 18·01. $C_{29}H_{23}O_5N_7$ requires N, 17·85 per cent.).

The above compound was heated with acetic acid for 5 to 6 hours when the solid gradually went into solution. On cooling the solution a brown precipitate was obtained which was crystallised from alcohol, in brown rectangles, m.p. 223°. (Found: N, 11·93. $C_{28}H_{18}O_4N_4$ requires N, 11·81 per cent.).

Phenanthraquinone di-β-naphthylaminoguanidine was obtained from the components and alcohol and crystallised from pyridine in golden yellow needles, m.p. 240°. (Found: N, 11·01. $C_{35}H_{24}ON_4$ requires N, 10·85 per cent.).

The above substance was heated in acetic acid suspension for 5 to 6 hours when the yellow colour was changed to grey. The separated solid was boiled with pyridine and crystallised from nitrobenzene as a red powder, m.p. above 300°. (Found: C, 91·44; H, 4·72; N, 4·38. $C_{25}H_{15}N$ requires C, 91·19; H, 4·56; N, 4·25 per cent.).

Phenanthraquinonemonoxime di-β-naphthylaminoguanidine, separated from alcohol as a yellow solid and crystallised from pyridine in golden yellow needles, m.p. 235°. (Found: N, 13·43. $C_{35}H_{25}ON_5$ requires N, 13·18 per cent.).

The above substance was heated with acetic acid for 6 to 7 hours. The solid that separated was crystallised from a mixture of alcohol and pyridine in yellow rectangles, m.p. 245°. (Found: C, 89·59; H, 4·86. $C_{35}H_{22}N_2$ requires C, 89·36; H, 4·68 per cent.).

2-*Nitrophenanthraquinone di-β-naphthylaminoguanidine* that separated from alcohol as a brown mass was crystallised from pyridine and water in brown rectangles, m.p. 200°. (Found: N, 12·69. $C_{35}H_{23}O_3N_5$ requires N, 12·48 per cent.).

The above substance was heated with acetic acid when there was a change of colour from yellow to violet. This was then boiled with pyridine and the residue crystallised from nitrobenzene in violet colour, m.p. 276°. (Found: N, 7·63. $C_{25}H_{14}O_2N_2$ requires N, 7·48 per cent.).

2:7-*Dinitrophenanthraquinone di-β-naphthylaminoguanidine* was obtained as a brown mass which was crystallised from pyridine in rectangles, m.p. 270°. (Found: N, 13·99. $C_{35}H_{22}O_5N_6$ requires N, 13·86 per cent.).

The above compound was heated for 6 to 7 hours when the colour changed from brown to black. This was then crystallised from nitrobenzene, m.p. above 300°. (Found: C, 71·83; H, 3·35. $C_{25}H_{13}O_4N_3$ requires C, 71·60; H, 3·10 per cent.).

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Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part VIII. The Stereoisomeric *d*-, *l*-, *dl*-, *p*-Phenylene-, 1 :4-Naphthylene-, *pp'*-Diphenylamine-, *pp'*-Diphenylmethane-bisiminocamphors ; *p*-Phenylene, *pp'*-Diphenylmethane-bisaminocamphors; *p*-Diphenylamineiminocamphors and *p*-Diphenylamineaminocamphors, and their Derivatives.

By Bawa Kartar Singh and Bhutnath Bhaduri.

Up till the year 1920, Forster's *p*-phenylenebisimino-*d*-camphor (*J. Chem. Soc.*, 1909, **95**, 942) was the classical instance, among carbon compounds, of a substance endowed with the highest rotatory power. The rotation constants of this compound were subsequently found to be exceeded by two substances prepared by one of us, namely, 1:4-naphthylenebisimino-*d*-camphor (*ibid*, 1920, **117**, 1599) and *pp'*-diphenylaminebisimino-*d*-camphor (*ibid*, 1921, **119**, 1975).

In the present communication, we have studied the imino-derivatives obtained from the condensation of the three stereoisomeric camphor-quinones (*d*-, *l*-, *dl*-) and the following aromatic amines: *p*-phenylene-diamine, 1:4-naphthylenediamine, *pp'*-diaminodiphenylamine, *pp'*-diaminodiphenylmethane and *p*-aminodiphenylamine.

The reduction of the imino to the amino-group in the molecule of this class of compounds is accompanied by a phenomenal depression in rotatory power, and this point has been emphasised in previous communications (*J. Chem. Soc.*, 1920, **117**, 980 ; 1921, **119**, 1971). But in the case of compounds now under discussion it had not hitherto been realised owing to the difficulty of reducing these imino-derivatives. It may be recalled that Forster (*loc. cit.*, p. 955)

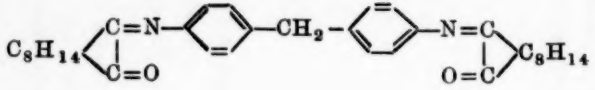
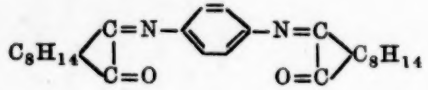
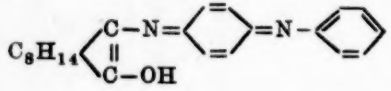
stated that "attempts to reduce this compound (*p*-phenylenebisimino-*d*-camphor) have failed." It is now found that this failure was due to the rapid oxidation of the reduced compound. We have succeeded in reducing this compound as well as the *l*- and *dl*-isomerides and isolating the bisamino-compounds as the dihydrochlorides. The free bases are precipitated by the addition of water to the alcoholic solution of the hydrochlorides, and melt at 204° (*d*- and *l*-), and at 215°-218° with decomposition (*dl*-). The stereoisomeric *pp'*-diphenylmethanebisiminocamphors and *p*-iminocamphordiphenylamines have also been reduced to the corresponding amino-compounds, but it was not found possible to effect the isolation of 1:4-naphthylenebisaminocamphors and *pp'*-diphenylaminebisaminocamphors in a pure state owing to their being oxidised very rapidly by air as is described in the experimental portion. The depression in the rotatory power which accompanies the reduction of the azethenoid groups in the molecule of the three compounds tabulated below is illustrated by the following measurements in pyridine.

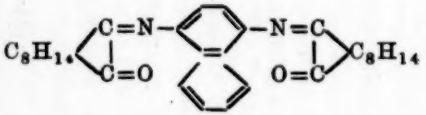
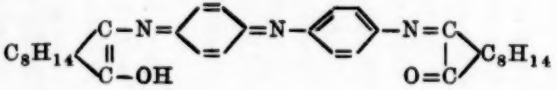
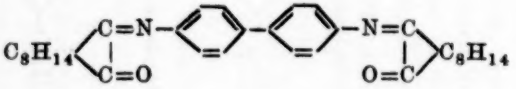
	$[M]^{35°}_{Hg\ green.}$	Difference.
p-Phenylenebisiminocamphor	8345°	8044°
p-Phenylenebisaminocamphor	301°	
pp'-Diphenylmethanebisiminocamphor	6016°	5696°
pp'-Diphenylmethanebisaminocamphor	320°	
p-Iminocamphordiphenylamine	8818°	8648°
p-Aminocamphordiphenylamine	170°	

It will be seen that these phenomenal changes in rotatory power effected by the such slight changes in molecular weight of these compounds are unknown among optically active substances, and they also far surpass in magnitude any changes in rotatory power in similar types of compounds already known (*J. Chem. Soc.*, 1920, 117, 980). It also illustrates the very great influence on rotatory power of conjugated double bonds when situated near the asymmetric centre.

The marked effect of unsaturation on rotatory power is brought out very clearly by counting the number of conjugated double bonds in the structural formulae of the six compounds shown in Table A, and comparing the specific rotatory power in different solvents. The rotatory power of compounds Nos. 1 to 5 increases as the number of conjugated double bonds in the molecule increases from 5 to 10. There is, however, no arithmetical proportion in these values. There is one marked exception to this rule in 1:4-naphthylenebisiminocamphor and *pp'*-bisiminocamphordiphenylamine. The former compound with nine conjugated double bonds has a higher specific rotatory power in pyridine than the latter which has ten. The molecular rotatory powers of the two compounds are, however, identical (Tables VI and VII). *pp'*-Diphenylenebisiminocamphor (Table A, No. 6) which has ten conjugated double bonds has higher rotatory power than *pp'*-diphenylmethanebisiminocamphor with five such bonds repeated twice, the conjugation being broken at the methane carbon atom, but it is less than that for the other four compounds (Nos. 2 to 5) with 7, 8, 9 and 10 such bonds respectively. This once more illustrates the effect of the optimum association of azethenoid groups, conjugated linkings and benzene rings within a given molecular compass. The narrower the molecular compass containing a given number of conjugated linkings, the greater is the rotation.

TABLE A.

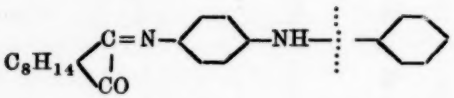
	Structural formula.	Name of conjugated double bonds.	$[\alpha]_D^{35°}$ Benzene (2·28)†	Chloroform (5·2)	Pyridine (12·4)	Acetone (21·5)	EtOH (25·8)	MeOH (31·2)
1.		5	905·3°	899·2°	921·5°	811·0°	830·6°	807·8°
2.		7	1567	1527	1562·6	1384·5	1344	1258
3.		8	1607	1693·5	2026	1667	2141	1898

4.		9	1902	1778	2908	2822	2621	2059
5.		10	2533	2382	2667	2629	2702	2517
6*		10	...	1140	...	...	...	1046

* Singh, Singh and Lal, *J. Chem. Soc.*, 1921, **119**, 1974.

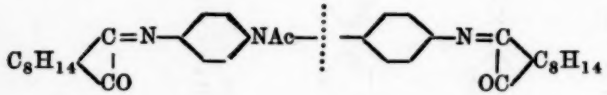
‡ Dielectric constant is given within brackets below the names of the solvents.

p-Iminocamphordiphenylamine has been assigned the structure represented by formula No. 3 (Table A), but its mode of formation leads to the following conventional formula,

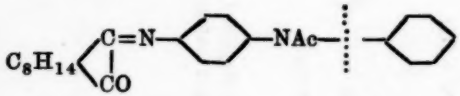


in which the conjugation is broken at the second benzene ring at its junction with the nitrogen atom of the amino-group, and shown by dotted line in the formula. This structure in which the conjugation between the two benzene rings is broken cannot be reconciled with its high rotatory power. But by depicting the quinonoid arrangement as in formula No. 3 (Table A), the conjugation in the molecule becomes continuous. The same explanation has already been advanced in the case of *pp'*-bisiminocamphordiphenylamine (*J. Chem. Soc.*, 1921, **119**, 1971). The double symmetric quinonoid arrangement as represented in formnla No. 5 (Table A) maintains an unbroken chain of conjugated double bonds which is not the case with the non-quinonoid arrangement, and not only does it explain the highest rotatory power which this compound possesses, but it also explains the flourescence which this substance exhibits in solution (*loc. cit.*).

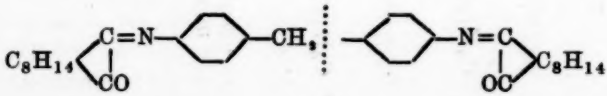
The acetyl derivatives of *p*-iminocamphordiphenylamine and *pp'*-bisiminocamphordiphenylamine have rotatory power which is of the same order as that of *pp'*-bisiminocamphordiphenylmethane. This suggests that the structure of the acetyl derivatives is, unlike the parent compounds, to be represented by formulae in which the conjugation is broken (as shown by dotted lines), as it, undoubtedly, is in *pp'*-bisiminocamphordiphenylmethane.



[α]Hg(green) in chloroform. 998°

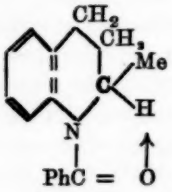


783°

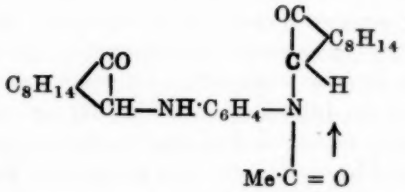


1189°

p-Phenylenebisaminocamphor is of interest on account of the reversal of sign of the rotatory power which takes place when the free base is converted into its acetyl derivative. The rotatory power of the optically active acetyl derivatives is opposite in sign in pyridine but not in chloroform (Table III). A reversal of sign on salt formation has been observed previously in solutions of the salts of brucine and coniine (Hilditch, *J. Chem. Soc.*, 1908, **93**, 700), and of nicotine (Nasini and Pezzolato, *Gazzetta*, 1893, **23**, 43; Lowry and Lloyd, *J. Chem. Soc.*, 1929, p. 1772), and a similar reversal occurs when tetrahydroquinaldine, $[\alpha]_D = +230°$ is converted into its benzoyl derivative, $[\alpha]_D = -61{\cdot}2°$ (Pope and Read, *J. Chem. Soc.*, 1910, **97**, 2206), or into other derivatives of a similar type (Pope and Winmill, *ibid*, 1912, **101**, 2309). A possible explanation of this reversal of the sign of rotatory power in benzoyltetrahydroquinaldine and acetyl-*p*-phenylenebisaminocamphor may be given by the postulation of a " dative bond " (Menzies, *Nature*, 1928, **121**, 457) between the acyl oxygen and the hydrogen atom attached to the asymmetric carbon atom (**C**) in the following formulae.



Benzoyltetrahydroquinaldine.



Acetyl-*p*-phenylenebisaminocamphor.

The reversal of sign of the rotatory power in these compounds may thus be associated with the saturation of a lone pair of electrons on the acyl oxygen. A similar explanation in the case of nicotine and its salts has been offered by Lowry and Lloyd (*loc. cit.*)

The Influence of Solvent on the Rotatory Power.—The solvents employed in this investigation in the decreasing order of their dielectric constants are methyl alcohol > ethyl alcohol > acetone > pyridine > chloroform > benzene. A reference to the tables of rotatory power (I to XII) will show that the sequence of solvents in order of decreasing (or increasing) rotatory power is quite different from that of their dielectric constants, and does not run strictly parallel with them even in one instance. In *p*-phenylenebisiminocamphor the sequence is obeyed except that pyridine and chloroform exhibit an

inverted relationship. In about fifty per cent. cases investigated, the order of rotatory power for the oxygen containing solvents is acetone >ethyl alcohol>methyl alcohol (see Tables I, II, VI, IX, and XII) which is the same as that of their dielectric constants but in a reverse order. This regularity has already been noticed with the derivatives of *d*-camphorimide and *d*-camphoramic acid (Singh and Puri, *J. Chem. Soc.*, 1926, **129**, 504). The solvent pyridine is, however, remarkable in one respect. The rotatory power of the mono- or bisiminocamphor derivatives is highest in this solvent, whereas it becomes lowest when these compounds are converted into the mono- or bisaminocamphor derivatives respectively.

The Influence of Chemical Constitution on Rotatory Dispersion.— Biot classified rotatory dispersions in two groups according as they did, or did not, obey the law of inverse squares $[\alpha]=k/\lambda^2$. The work of Lowry and his school has shown that this law is never disobeyed exactly, although some substances such as sodium tartrate (Lowry and Austin, *Phil. Trans.*, 1922 A, **222**, 249) and octyl oxalate (Lowry and Richards, *J. Chem. Soc.*, 1924, **125**, 1593) obey it very nearly. Lowry (*Trans. Faraday Soc.*, 1914, **10**, 96) has classified rotatory dispersions as " simple " and " complex " according as they can or cannot be expressed by the equation $[\alpha]=k/(\lambda_2-\lambda_0^2)$ This equation which differs from Biot's equation only by the addition of λ_0^2 was deduced by Drude in 1898 for rotatory dispersion in transparent media; it does not, therefore, apply to the absorbent media studied by Cotton (*Compt. rend.*, 1895, **120**, 949, 1044; *Ann. chim. Phys.*, 1896, *vii*, **8**, 347) where anomalies are observed on passing through the region of absorption. The " simple " formula is valid for a large number of secondary alcohols containing one asymmetric carbon atom (Lowry and Dickson, *J. Chem. Soc.*, 1913, **103**, 1067; Lowry and Richard, *loc. cit.*). Among numerous other substances which obey the " simple " dispersion law are sucrose, camphorquinone (Lowry and Richards, *ibid*, 1924, **125**, 2511), and nicotine (Lowry and Singh, *Compt. rend.*, 1925, **181**, 909; Lowry and Lloyd, *loc. cit.*).

The rotatory dispersion of camphor and most of its derivatives cannot be expressed by the one-term equation of Drude. It is therefore not " simple " but " complex ". In nearly every case however, it can be expressed by using two terms of Drude's equation (Lowry and Cutter, *J. Chem. Soc.*, 1925, **127**, 604), although the dispersions are sometimes normal as in the case of camphor itself, and

sometimes anomalous as in the case of α'-bromocamphor the dispersion curve of which is unique as it shows all the three characteristic anomalies simultaneously, namely, an inflexion, a maximum and a reversal of sign.

The substances investigated in the present paper show all the three types of rotatory dispersion, namely " simple," " complex " and " anomalous ". The graphical method of analysis which consists in plotting $^1/_\alpha$ against λ^2 was applied in every case. Those cases in which straight lines were not obtained were at once shown to conform to complex or anomalous rotatory dispersion. In a few cases straight lines were obtained which pointed that they may represent simple rotatory dispersion. These were then analysed by the more exact numerical method, which consists in working out a dispersion formula based on the one-term equation of Drude, $[\alpha]=k/(\lambda^2-\lambda_o{}^2)$ and then seeing whether the observed and calculated rotations show *systematic* errors, or *casual* errors. As our observations were made with three or four wave-lengths only, no attempt was made to find a rotatory dispersion formula involving two-terms of Drude's equation. The results of our analysis in the above mentioned way have shown that the substances which exhibit simple rotatory dispersion are the acetyl derivatives of *pp'*-diphenylaminebisiminocamphors (Table VI), *p*-diphenylamineaminocamphors (Table IX) in all the solvents, and diacetyl derivatives of *p*-diphenylamineaminocamphors in all the solvents except pyridine (Table X), in which the differences in the observed and calculated values of rotatory power are greater than the experimental errors. In the same category may be perhaps, included *pp'*-diphenylmethanebisiminocamphors in acetone and methyl alcohol (Table XI) and their reduction products namely, *pp'*-diphenylmethanebisaminocamphors in acetone, methyl alcohol and ethyl alcohol (Table XII). The monoacetyl derivatives of *p*-phenylenebisaminocamphors show anomalous dispersion in pyridine (Table III) ; the dispersion curves cut the axis of zero rotation at some wave-length lying between Hg_{violet} and Hg_{green}, and thus exhibit one of the three characteristic anomalies, namely, reversal of sign of rotatory power. In chlorofom solution it however, shows complex rotatory dispersion, to which type also the remaining substances conform.

It will be further observed that there is no connection between the number of asymmetric centres in a molecule and the type of rotatory dispersion which it exhibits. Camphorquinone and camphor

contain two asymmetric carbon atoms but the rotatory dispersion of the former compound is "simple", whereas that of the latter "complex" (*loc. cit.*). The optically active *pp'*-diphenylaminebisiminocamphors and their acetyl derivatives have four asymmetric carbon atoms but the rotatory dispersion of the former compound is "complex", whereas that of the latter "simple" The *pp'*-diphenylmethanebisaminocamphors have six asymmetric carbon atoms, but their rotatory dispersion is "simple" in acetone, methyl alcohol and ethyl alcohol, and "complex" in chloroform, benzene, and pyridine. The monoacetyl derivatives of *p*-phenylenebisaminocamphors contain also six asymmetric carbon atoms, but the rotatory dispersion is "complex" in chloroform, and anomalous in pyridine.

The last examples cited also show that the type of rotatory dispersion of a molecule is dependent on the nature of the solvent in which it is dissolved. The dispersion constant λ^2_0, in the one term Drude's equation enables the value of λ_0, the wave-length of the absorption band in the ultra-violet, to be calculated. This value varies from about 3500 to 3700 A. U. for the acetyl derivatives of the optically active *pp'*-diphenylaminebisiminocamphors in different solvents. This indirect determination of the wave-length of the ultra-violet absorption band (head) should be compared with that obtained by direct measurement. It could thus be used in testing the validity of the application of Drude's equation for rotatory dispersion. It is hoped to make this comparison in a later communication. The values of λ_0 for other substance showing "simple" rotatory dispersion are given in the tables of rotations.

The Physical Identity of Enantiomers.—Since the discovery of molecular asymmetry by Pasteur, and later by Van't Hoff and Le Bel, it has always been *assumed* that apart from the sign of rotation, the physical properties of the dextro- and laevo-enantiomers are identical, whereas these properties are different for racemic forms.

About four years ago, we commenced the present investigation, which had, as one of its objects, the experimental confirmation (or otherwise) of the above mentioned assumption, namely, the equality in the numerical value of the rotatory power of the opposite active forms. The compounds described in this paper possess very high rotatory power; they, therefore, lend themselves remarkably well for this comparison. A reference to Tables I to XII will show that the differences in the values of rotatory power of the dextro- and

laevo-forms are very small indeed, and are well within the experimental errors. So far as these compounds are concerned, it may be safely concluded that the assumption of the equality of rotatory power of enantiomers is not disproved. On the other hand it may be claimed that the results of the experiments now described fully support it.

The melting points of the racemic forms of the substances are different from those of the opposite active forms. Where the melting point of the inactive form is higher than that of the active, there can be no doubt that the inactive form is, in the solid state, a true racemate. But where the racemic form has lower melting point, further experiments are required to settle whether it is a true compound, or a mixture of equal proportions of the two enantiomers. If the melting point of the racemic form can be lowered by the addition of the optically active form, there can be no doubt that the racemic form is not a mixture, but a true racemate. The melting points of the racemic forms of 1:4-naphthylenebisiminocamphor and *pp'*-diphenylmethanebisiminocamphor are depressed by 2—3° on the addition of about 10 per cent. of their dextro-isomerides, which points them to be true racemates. The case is quite different with the racemic form of *p*-phenylenebisiminocamphor, as its melting point is continuously raised by the addition of gradually increasing quantities of the *d*-isomeride (*vide* Experimental). This shows that the racemic form of this substance is a mixture.

Experimental.

p-*Phenylenebisimino*-d-*camphor* (*Formula* 2, Table A).

This substance was prepared in a slightly different way from that of Forster's (*J. Chem. Soc.*, 1909, **95**, 942) with improved yield. *d*-Camphorquinone (2 mols.), *p*-phenylenediamine hydrochloride (1 mol.) and excess of freshly fused sodium acetate were heated on a water-bath for 8 hours. The mass was extracted with hot alcohol, and precipitated with water. It was crystallised out of alcohol, as golden yellow needles melting at 259°-260°, (yield, 60%). The substance is freely soluble in chloroform, benzene and pyridine; less readily in acetone, less so in ethyl alcohol and methyl alcohol; slightly soluble in ether and insoluble in water. (Found: N, 7·05; $C_{26}H_{32}O_2N_2$ requires N, 6·93 per cent.). The order of rotatory power

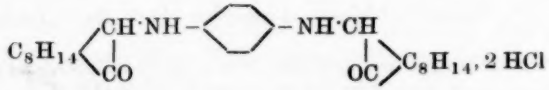
in different solvents (see Table I) is as below:—Benzene>pyridine>chloroform>acetone>ethyl alcohol>methyl alcohol. *p*-Phenylenebisimino-*l*-camphor was obtained from *l*-camphorquinone in the same way. It had the same melting point, solubility, and order of rotatory power (see Table I) as the *d*-isomeride. (Found: C, 77·22; H, 8·15. $C_{26}H_{32}O_2N_2$ requires C, 77·23; H, 7·92 per cent).

p-Phenylenebisimino-*dl*-camphor was prepared from *dl*-camphorquinone in the same way as the corresponding *d*- and *l*-compounds, and crystallises as yellow needles melting at 252-253°. (Found: N, 7·15. $C_{26}H_{32}O_2N_2$ requires N, 6·93 per cent.). The following table of mixed melting points of *d*- and *dl*-isomerides shows that the substance is probably a racemic mixture and not a racemic compound.

Proportion of *dl*-isomeride.	Proportion of *d*-isomeride.	M.p.
100%	Nil	252°-53°
90	10%	253°-54°
50	50	253°-54°
15	85	254°-55°
5	95	257°-58°
Nil	100	259°-60°

A mixture of equal quantities of *d*- and *l*-isomerides melts at 252-53°.

p-*Phenylenebisamino*-d-*camphor Dihydrochloride*.



p-Phenylenebisimino-*d*-camphor (1 g.) dissolved in 100 c.c. of benzene was shaken with 100 c.c. of 10 per cent. caustic potash solution in presence of zinc dust (5 g.) continuously until the benzene layer was colourless (10 to 12 hours). It was filtered off free from zinc dust, the benzene layer separated and washed with water till free from alkali. The solution turned pink immediately on exposure. The operations were completed as quickly as possible as the substance is liable to be oxidised rapidly in solution. Dry hydrochloric

acid gas was then passed through the benzene solution when a gelatinous mass (pinkish) was precipitated: this was filtered off, washed with benzene and dried (yield, 85 to 90 per cent.).

It has no sharp melting point; it darkens from 217° melting completely at 225°. It is easily soluble in ethyl alcohol but the free base is liberated from the salt when it is shaken with water. (Found: Cl, 14·50. $C_{26}H_{38}O_2N_2Cl_2$ requires Cl, 14·76 per cent.).

p-*Phenylenebisamino*-d-*camphor*.—The dried hydrochloride was dissolved in alcohol (the solution turning violet) and precipitated with water. It was crystallised from hot alcohol as white prisms melting at 204°. The yield was 65-70 per cent.

It is very readily soluble in pyridine, chloroform, benzene and acetone; less so in ethyl alcohol and methyl alcohol, slightly soluble in ether and insoluble in water. (Found: C, 76·81; H, 8·85. $C_{26}H_{36}O_2N_2$ requires C, 76·47; H, 8·82 per cent.).

The order of rotatory power in solvents (see Table II) is as below: Chloroform > benzene > acetone > ethyl alcohol > methyl alcohol > pyridine. p-*Phenylenebisamino*-l-*camphor dihydrochloride* was prepared in the same way as the corresponding dextro-isomeride and has similar properties. (Found: Cl, 14·69. $C_{26}H_{38}N_2O_2Cl_2$ requires Cl, 14·76 per cent.). p-*Phenylenebisamino*-l-*camphor* was prepared in the same way as the corresponding dextro-compound and has the same melting point and solubility. (Found: C, 76·26; H, 9·10. $C_{26}H_{36}N_2O_2$ requires C, 76·47; H, 8·82 per cent.).

The values of rotatory power of the *l*-isomeride are identical with those of the *d*- compound within experimental error (see Table II).

p-*Phenylenebisamino*-dl-*camphor dihydrochloride* was prepared in the same way as the corresponding *d*-and *l*-isomerides. (Found: Cl, 14·63. $C_{26}H_{38}O_2N_2Cl_2$ requires Cl, 14·76 per cent.).

p-*Phenylenebisamino*-dl-*camphor* was prepared in the same way as the corresponding dextro- and laevo-compounds but unlike them it has no sharp melting point. It begins to turn yellow from 198°, completely yellow at 210°, blackening begins from 215°, melting completely at 220°. It is soluble in benzene and chloroform; less so in ethyl alcohol and methyl alcohol and sparingly soluble in ether. (Found: C, 76·40; H, 9·12. $C_{26}H_{32}O_2N_2$ requires C, 76·47; H, 8·82 per cent.).

Monoacetyl Derivative of p-*Phenylenebisamino*-d-*camphor.*—*p*-Phenylenebisamino-*d*-camphor (1 g.) was heated with acetic anhydride (1·2 g.) at 195-200° for 20-25 minutes and poured into water while still hot when it solidified. It was crystallised out of 70 per cent. alcohol as white silky needles (yield, 50%). It has no sharp melting point; darkening from 245°, it shows signs of melting at 250° and completely melts at 253-54°. It is readily soluble in chloroform and pyridine, less so in benzene and acetone; sparingly soluble in alcohol and insoluble in water. (Found: C, 74·59; H, 8·78. $C_{28}H_{38}O_3N_2$ requires C, 74·66; H, 8·44 per cent.). Found: acetyl (hydrolysis method)=8·49 ; acetyl (Perkin's method)=9·78. $C_{28}H_{38}O_3N_2$ (monoacetyl) requires acetyl, 9·50 per cent.).

The rotatory power was determined in chloroform and pyridine only (see Table III) as the solubility in other solvents was too small. The *l*-isomeride was prepared in the same way and has similar properties. (Found: C, 74·54; H, 8·68. $C_{28}H_{38}O_3N_2$ requires C, 74·66; H, 8·44 per cent.).

The sign of rotatory power for the *d*- and *l*-isomerides is opposite in pyridine solution for Hg_{green} Hg_{yellow} and Na_D lines but same for Hg_{violet} (see Table III).

The *monoacetyl* derivative of *p*-phenylenebisamino-*dl*-camphor was prepared and crystallised in the same way as the corresponding optically active isomerides and has similar solubility but unlike them, melts at 192-93° (white crystals). (Found: C, 74·50 ; H, 8·66. $C_{28}H_{38}O_3N_2$ requires C, 74·66; H, 8·44 per cent.).

1:4-*Naphthylenebisimino*-d-*camphor* (*Formula* 3, Table A),

It was prepared according to the method given by one of us (Singh and Singh, *J. Chem. Soc.*, 1920, **117**, 1601) and obtained as red plates melting at 220-22°. It is freely soluble in organic media excepting ether which dissolves the substance only sparingly. (Found: C, 79·16; H, 7·75. $C_{30}H_{34}O_2N_2$ requires C, 79·29; H, 7·49 per cent.).

The substance is thus identical with that already described (*loc. cit.*) except that the melting point recorded there is 8° higher, which is obviously a misprint. The order of rotatory power in solvents (see Table IV) is as follows: Pyridine > ethyl alcohol >acetone > methyl alcohol > benzene > chloroform. 1:4-*Naphthylenebisimino*-l-*camphor* was prepared in the same way as the corresponding *d*-isomeride and has the same melting point and solubility. (Found:

C, 79·10; H, 7·39. $C_{30}H_{34}O_2N_2$ requires C, 79·29; H, 7·49 per cent.).

The rotatory power is identical with that of the *d*-isomeride within experimental error (see Table IV).

1:4-*Naphthylenebisimino*-dl-*camphor* was prepared in a similar way as the corresponding *d*- and *l*-compounds and had similar solubility but melts at 213°-14° (red plates). (Found: C, 78·89; H, 7·51. $C_{30}H_{34}O_2N_2$ requires C, 79·29; H, 7·49 per cent.).

All attempts to isolate the reduced product of 1: 4-naphthylenebisiminocamphor have failed for although the ethereal solution of the substance becomes colourless when shaken with 10 per cent. potassium hydroxide solution and zinc dust, it turned red immediately on exposure to air and a substance of varying composition and melting point could only be isolated. The rapid change could not be checked even when all the operations such as filtration, evaporation, etc., were conducted in an inert atmosphere of hydrogen or carbon dioxide. The hydrochloride as formed by passing dry hydrochloric acid gas through the reduced ethereal solution had also a varying composition (always showing a higher chlorine content); the free base liberated by the addition of ammonia was very unstable changing from grey to brown very rapidly (specially in solution) and when it was tried to crystallise out of alcohol, a red substance (m.p. 180°-85°) was obtained.

pp′-*Diphenylaminebisimino*-d-*camphor* (*Formula* 5, Table A).

This substance was prepared according to the method given by one of us (Singh, Singh and Lal, *J. Chem. Soc.*, 1921, **119**, 1975) with improved yield and formed greenish-yellow prisms melting at 212°-13° (yield, 60 per cent.).

It is freely soluble in organic media excepting ether which dissolves it only sparingly. (Found: C, 77·43; H, 7·70. $C_{32}H_{37}O_2N_3$ requires C, 77·58; H, 7·47 per cent.).

The order of rotatory power in different solvents (see Table V) is: ethyl alcohol>pyridine>acetone>benzene, >methyl alcohol> chloroform. The *l*-isomaride was prepared in a similar way from *l*-camphorquinone and has the same melting point and solubility in different organic media. (Found: C, 77·51; H, 7·73. $C_{32}H_{37}O_2N_3$ requires C, 77·58; H, 7·47 per cent.).

The rotatory power is identical with that of the *d*-isomeride (Table V).

pp'-*Diphenylaminebisimino*-dl-*camphor* was prepared and crystallised in the same way as the corresponding optically active isomerides (much more tarry matter separated in this case which was washed off with a little ether, the last traces being removed by boiling the alcoholic solution with a trace of animal charcoal). It crystallised as scarlet red plates melting at 144°-45°. (Found: N, 8·58. $C_{32}H_{37}O_2N_3$ requires N, 8·49 per cent.).

The acetyl derivative of *pp'*-diphenylaminebisimino-*d*-camphor was prepared by heating *pp'*-diphenylaminebisimino-*d*-camphor (1 g.) with acetic anhydride (2 g.) at 170-180° for an hour, and obtained as greenish-yellow plates melting at 227° (yield, 0·6 g.). It is readily soluble in chloroform, benzene, acetone, and pyridine; less so in ethyl alcohol and methyl alcohol and insoluble in water. (Found: C, 76·13; H, 7·52. $C_{34}H_{39}O_3N_3$ requires C, 75·98; and H, 7·26 per cent.). The order of rotatory power (Table VI) is as below: benzene > pyridine > chloroform > acetone > ethyl alcohol > methyl alcohol. Attempts to prepare a methyl derivative of *pp'*-diphenylaminebisimino-*d*-camphor have failed.

The corresponding *l*-isomride was prepared in a similar way *pp'*-diphenylaminebisimino-*l*-camphor and has the same melting point and solubility in different organic media. (Found: C, 75·86; H, 7·55. $C_{34}H_{39}O_3N_3$ requires C, 75·98; H, 7·26 per cent.). The rotatory power is identical with the dextro-isomeride in all solvents (Table VI).

pp'-Diphenylaminebisimino-*dl*-camphor could not be acetylated.

p-*Imino*-d-*camphordiphenylamine* (*Formula* 3, Table A).

d-Camphorquinone (1 mol.) was heated with *p*-aminodiphenylamine hydrochloride (1 mol.) with fused sodium acetate at about 75° for 4-5 hours. The mass was extracted with alcohol and precipitated with water. The precipitate crystallised as yellowish-green needles melting at 134°-35° (yield, 70—80%). It is readily soluble in different organic media. (Found: C, 79·44; H, 7·46. $C_{22}H_{24}ON_2$ requires C, 79·52; H, 7·23 per cent.).

The order of rotatory power (see Table VII) is as below: ethyl alcohol > pyridine > methyl alcohol > chloroform > acetone > benzene.

p-*Imino*-l-*camphordiphenylamine* was prepared in a similar way as the corresponding dextro-isomeride and has the same melting point and similar solubility. (Found: C, 79·38; H, 7·54.

$C_{22}H_{24}ON_2$ requires C, 79·52; H, 7·23 per cent.). The rotatory power in different solvents is identical in numerical value with that of the *d*-isomeride (see Table VII).

p-*Imino*-d-*camphordiphenylamine* was prepared in the same way as the corresponding *d*- and *l*-compounds and crystallised as yellowish-orange shining plates melting at 144°-45°. It is readily soluble in different organic media. (Found: C, 79·52 ; H, 7·48. $C_{22}H_{24}ON_2$ requires C, 79·52; H, 7·23 per cent.).

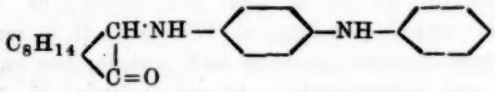
The *acetyl* derivative of *p*-imino-*d*-camphordiphenylamine was prepared by heating p-imino-*d*-camphordiphenylamine with acetic anhydride at 165°-170° for an hour, and was obtained as greenish-yellow plates melting at 163°-64° (yield, 60—65%). It is readily soluble in chloroform, benzene; less so in ethyl alcohol and methyl alcohol. (Found: C, 76·88; H, 7·22. $C_{24}H_{26}O_2N_2$ requires C, 77·00; H, 6·95 per cent.). The order of rotatory power in different solvents (Table VIII) is—

benzene $>$ pyridine $>$ chloroform $>$ ethyl alcohol, acetone $>$ methyl alcohol. The *l*-isomeride was prepared in a similar way from *p*-imino-*l*-camphordiphenylamine and has the same melting point and solubility. (Found: C, 76·86; H, 7·27. $C_{24}H_{26}O_2N_2$ requires C, 77·00; H, 6·95 per cent.). The numerical value of the rotatory power in different solvents is identical with that of the *d*-compound (Table VIII).

The *acetyl* derivative of *p*-imino-*dl*-camphordiphenylamine was prepared in the same way as the corresponding dextro-and laevo-isomerides and crystalylised as light green plates melting at 153°-54°. It is readily soluble in different organic media. (Found: C, 76·91; H, 7·26. $C_{24}H_{26}O_2N_2$ requires C, 77·00; H, 6.95 per cent.).

Attempts to prepare a methyl derivative of *p*-imino-*d*-camphordiphenylamine have failed.

p-*Amino*-d-*camphordiphenylamine*,



was prepared in the usual way, by the reduction of *p*-imino-*d*-camphordiphenylamine (in ether solution) with 10 per cent. potassium hydroxide solution in presence of zinc dust, and was obtained as shining white plates melting at 121°-22°. It is readily soluble

in different organic media. (Found: C, 78·96; H, 8·10. $C_{22}H_{26}ON_2$ requires C, 79·05; H, 7·79 per cent.). The order of rotatory power is different solvents (see Table IX) is as follows:

benzene > chloroform > acetone > ethyl alcohol > methyl alcohol > pyridine.

p-*Amino*-l-*camphordiphenylamine* was prepared in a similar way as the corresponding *d*-isomeride and has the same melting point and solubility. (Found: C, 78·76; H, 7·99. $C_{22}H_{26}ON_2$ requires C, 79·05; H, 7·79 per cent.).

The rotatory power in different solvents is identical with that of the *d*-isomeride (see Table IX).

p-*Amino*-dl-*camphordiphenylamine* was prepared in the same way as the other two isomerides and crystallised as shining plates (white) melting at 93-94°. It is readily soluble in different organic media. (Found; C, 78·56 ; H, 8·19. $C_{22}H_{26}ON_2$ requires C, 79·05; H, 7·79 per cent.).

The *diacetyl* derivative of *p*-amino-*d*-camphordiphenylamine was prepared by heating *p*-amino-*d*-camphordiphenylamine (1 g.) with acetic anhydride (3 g.) at 140-150° for 20 minutes, and obtained as white prisms melting at 190-91° (yield, 0·6 g.). (Found: C, 74·49; H, 7·52. $C_{26}H_{30}O_3N_2$ requires C, 74·64; H, 7·18 per cent.).

The order of rotatory power in four solvents (see Table X) is benzene > chloroform > acetone > pyridine.

The rotatory power in ethyl alcohol and methyl alcohol was not determined owing to its small solubility in these solvents. The l-*isomeride* was prepared in a similar way from *p*-amino-*l*-camphordiphenylamine and has the same melting point and solubility. (Found: C, 74·63; H, 7·78. $C_{26}H_{30}O_3N_2$ requires C, 74·64; H, 7·18 per cent.).

The rotatory power is indentical in numerical value with that of the *d*-isomeride (see Table X).

The *monoacetyl* derivative of *p*-amino-*d*-camphordiphenylamine was prepared by heating *p*-amino-*dl*-camphordiphenylamine with acetic anhydride at 160-170° for 30 minutes, and obtained as light white microscopic crystals melting at 175°-76°. It is readily soluble in chloroform, benzene, pyridine and acetone; less readily in ethyl alcohol and methyl alcohol. (Found: C, 76·34; H, 7·94. $C_{24}H_{28}O_2N_2$ requires C, 76·60; H, 7·44 per cent.).

It is rather curious that the racemic compound forms only a monoacetyl derivative and the corresponding *d*- and *l*-compounds give diacetyl derivatives.

pp′-*Diphenylmethanebisimino*-d-*camphor* (*Formula* 1, Table A).

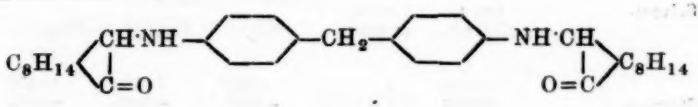
d-Camphorquinone (2 mols.) was heated on the water-bath with *pp′*-diaminodiphenylmethane (1 mol.) in presence of fused sodium sulphate for 7 to 8 hours. The mass was extracted with alcohol and precipitated with water. It was crystallised out of dilute alcohol as yellow prisms melting at 203-204° (yield, 60 per cent.). It is readily soluble in alcohol, chloroform, benzene, acetone and pyridine; less readily in ether and insoluble in water. (Found: C, 79·97; H, 7·90. $C_{33}H_{38}O_2N_2$ requires C, 80·16; H, 7·69 per cent.).

The order of rotatory power in different solvents (Table XI) is pyridine > benzene > chloroform > ethyl alcohol > acetone > methyl alcohol. The *l*-isomeride was prepared in a similar way and has the same melting point and solubility. (Found: C, 80·02; H, 7·99. $C_{33}H_{38}O_2N_2$ requires C, 80·16; H, 7·69 per cent.).

The magnitude of the rotatory power is identical with that of the *d*-compound (Table XI).

pp′-*Diphenylmethanebisimino*-dl-*camphor* was prepared in a similar way as the corresponding *d*- and *l*- compounds and crystallised as yellow prisms melting at 200-201°. (Found: C, 79·86; H, 7·82. $C_{33}H_{38}O_2N_2$ requires C, 80·16; H, 7·82 per cent.).

pp′-*Diphenylmethanebisamino*-d-*camphor*,



was prepared in the usual way by the reduction of *pp′*-diphenylmethanebisimino-*d*-camphor with 10 per cent. potassium hydroxide solution in presence of zinc dust, and was obtained as light cream-coloured crystals (probably prisms) melting at 182° (yield, 50 per cent.). It is readily soluble in chloroform, benzene, pyridine, ether and acetone; less so in ethyl alcohol, sparingly soluble in methyl alcohol and insoluble in water. (Found: C, 78·89; H, 8·54. $C_{33}H_{42}O_2N_2$ requires C, 79·51; H, 8·44 per cent.).

The order of rotatory power in different solvents (Table XII) is benzene >chloroform > acetone > ethyl alcohol > methyl alcohol > pyridine.

The l-*isomeride* was prepared in a similar way from *pp′*-diphenyl methanebisimino-*l*-camphor and has the same melting point and

solubility. (Found: C, 79·16; H, 8·76. $C_{33}H_{42}O_2N_2$ requires C, 79·51; H, 8·44 per cent.).

The value of the rotatory power in different solvents is identical with that of the *d*-compound (Table XII).

*pp'-Diphenylmethanebisamino-*dl*-camphor* was prepared in a similar way as the two optically active isomerides and crystallised as light cream-coloured crystals melting at 164°-65°. (Found: C, 79·60; H, 8·59. $C_{33}H_{42}O_2N_2$ requires C, 79·51; H, 8·44 per cent.).

Attempts to isolate the acetyl derivative of *pp'*-diphenylmethanebisamino-*d*-camphor have failed.

The rotatory power determinations recorded in Tables I to XII, were made in a 2 dcm. jacketed tube and the temperature was maintained at 35° throughout these observations. $Hg_{vio.}$ $Hg_{gr.}$ Hg_{yel}. and Na_D refer to the violet mercury line 4358, the green mercury line 5461, the yellow mercury line 5780, and the yellow sodium line 5893 respectively. In the case of compounds, which show simple rotatory dispersion, the value of λ_0 has been calculated from the dispersion formula, and is expressed as μ or 10^{-4} cm.

TABLE I.

p-Phenylenebisiminocamphor.

Solvent.	Concentration: g./100 c.c.	Dextro, laevo, or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Benzene	0·0784	*d*	+6331°	+6569°	+8476°
	0·0696	*l*	−6387	−6585	−8472
		Mean	6359	6577	8474
Pyridine	0·0736	*d*	+6313	+6503	+8345
	0·0792	*l*	−6270	−6476	−8338
		Mean	6292	6490	8342
Chloroform	0·0724	*d*	+6169	+6387	+8173
	0·0716	*l*	−6152	−6404	−8212
		Mean	6160	6395	8193
Acetone	0·0780	*d*	+5593	+5680	+7171
	0·0756	*l*	−5656	−5712	−7191
		Mean	5624	5696	7181
Ethyl alcohol	0·0740	*d*	+5430	+5543	+7150
	0·0840	*l*	−5410	−5531	−7118
		Mean	5420	5537	7134
Methyl alcohol	0·0704	*d*	+5082	+5224	+6690
	0·0700	*l*	−5078	−5224	−6698
		Mean	5080	5224	6694

TABLE II.

p-Phenylenebisaminocamphor.

Solvent.	Concentration : g./100 c.c.	Dextro, laevo, or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Chloroform	0·4080	*d*	+470·0°	+534·9°	+610·0°
	0·4184	*l*	−468·1	−516·9	−604·6
		Mean	469·05	525·0	607·3
Benzene	0·4084	*d*	+439·4	+499·9	574·2
	0·4168	*l*	−445·4	−494·4	−577·7
		Mean	442·4	497·1	575·9
Acetone	0·4136	*d*	+426·9	+481·5	+550·8
	0·4184	*l*	−419·4	−477·8	−546·2
		Mean	423·1	479·6	548·5
Ethyl alcohol	0·1660	*d*	+331·4	+417·9	+504·0
	0·1700	*l*	−324·1	−4[illegible]8·0	−492·0
		Mean	327·7	412·9	498·0
Methyl alcohol	0·1688	*d*	+302·1	+326·3	+398·8
	0·1708	*l*	−298·5	−334·5	−406·2
		Mean	300·3	330·4	402·5
Pyridine	0·4136	*d*	+236·7	+256·5	+300·9
	0·4060	*l*	−243·8	−248·3	−293·6
		Mean	240·2	252·4	297·2

Concentration of the substance in ethyl alcohol and methyl alcohol was not same as in other solvents, the substance being not so readily soluble in them.

TABLE III.

Monoacetyl Derivative of p-*Phenylenebisaminocamphor.*

Solvent.	Concentration : g./100 c.c.	Dextro, laevo or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$	[M] $Hg_{vio.}$
Chloroform	0·4352	*d*	+124·06°	+160·47°	+201·64°	...
	0·4444	*l*	−126·58	−161·95	−202·59	...
		Mean	125·32	161·21	202·12	...
Pyridine	0·4148	*d*	−108·45	−86·85	−59·67	+54·22°
	0·4164	*l*	+97·24	+81·04	+59·4	−48·6
		Mean	102·85	83·95	59·54	51·41

The substance was difficultly soluble in other solvents ; hence readings could not be taken in them.

TABLE IV.

1:4-*Naphthylenebisiminocamphor.*

Solvent.	Concentration g./100 c.c.	Dextro, laevo or mean.	[M] Na_D	[M] $Hg_{yel.}$
Pyridine	0·0141	*d*	+13200°	+14170°
	0·0155	*l*	−13320	−14060
		Mean	13260	14115
Ethyl alcohol	0·0145	*d*	+11899	+12526
	0·0150	*l*	−11960	−12560
		Mean	11930	12543
Acetone	0·0155	*d*	+10540	+11570
	0·0149	*l*	−10520	−11430
		Mean	10530	11500
Methyl alcohol	0·0153	*d*	+9348	+10390
	0·0148	*l*	−9356	−10280
		Mean	9352	10335
Benzene	0·0142	*d*	+8634	+9431
	0·0150	*l*	−8788	−9535
		Mean	8711	9483
Chloroform	0·0149	*d*	+8074	+8837
	0·0152	*l*	−8215	−8812
		Mean	8145	8825

Hg_{green} line could not be read through these solutions.

TABLE V.

pp′-*Diphenylaminebisiminocamphor.*

Solvent.	Concentration : g./100 c.c.	Dextro, laevo or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Ethyl alcohol	0·0148	*d*	+13350°	+14030°	+19050°
	0·0151	*l*	−13080	−13930	−19010
		Mean	13230	13980	19030
Pyridine	0·0150	*d*	+13200	+13860	+18810
	0·0151	*l*	−13110	−13770	−18690
		Mean	13155	13815	18750
Acetone	0·0154	*d*	+13020	+13660	+18640
	0·0155	*l*	−12770	−13570	−18490
		Mean	12895	13615	18565
Benzene	0·0150	*d*	+12530	+13200	+18150
	0·0155	*l*	−12290	−13090	−18040
		Mean	12410	13145	18095
Methyl alcohol	0·0147	*d*	+12460	+13130	+18020
	0·0148	*l*	−12540	−13210	−18060
		Mean	12500	13170	18040
Chloroform	0·0149	*d*	+11790	+12510	+17270
	0·0146	*l*	−11690	−12370	−17120
		Mean	11740	12440	17195

TABLE VI.

Acetyl Derivative of pp'-*Diphenylaminebisiminocamphor.*

Chloroform. $[\alpha]=\frac{168{\cdot}3}{\lambda^2-0{\cdot}1292}$; $[M]=5{\cdot}37[\alpha]$; $\lambda_0=0{\cdot}3594$.

	Concentration : g./100 c.c.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Dextro	0·0912	+4181°	+4393°	+5357°
Laevo	0·0901	−4172	−4351	−5364
Mean (obs.)	...	4176·5	4372	5360·5
Calc.	...	4143	4411	5348
Diff.	...	+33·5	−39·0	+ 12·5

Ethyl alcohol. $[\alpha]=\frac{151{\cdot}4}{\lambda^2-0{\cdot}1224}$; $[M]=5{\cdot}37[\alpha]$; $\lambda_0=0{\cdot}3499$.

Dextro	0·0910	+3629°	+3806°	+4633°
Laevo	0·0904	−3666	−3815	−4650
Mean (obs.)	...	3647·5	3810·5	4641·5
Calc.	...	3615	3841	4624
Diff.	...	+ 32·5	− 30·5	+ 17·5

Methy lalcohol. $[\alpha]=\frac{135{\cdot}3}{\lambda^2-0{\cdot}1347}$; $[M]=5{\cdot}37\,[\alpha]$; $\lambda_0=0{\cdot}3670$.

Dextro	0·0917	+3456	+3631	+4450
Laevo	0·0900	−3431	−3630	−4445
Mean (obs.)	...	3443·5	3630·5	4447·5
Calc.	...	3418	3643	4443
Diff.	...	+ 25·5	− 22·5	+ 4·5

TABLE VI—*contd.*

Acetyl Derivative of pp'-Diphenylaminebisiminocamphor.

Acetone. $[\alpha] = \frac{151{\cdot}6}{\lambda^2 - 0{\cdot}1343}$; $[M] = 5{\cdot}37\,[\alpha]$; $\lambda_0 = 0{\cdot}3664$.

	Concentration : g./100 c. c.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Dextro	0·0919	+3856°	+4060°	+4966°
Laevo	0·0902	−3807	−4048	−5000
Mean (obs.)	...	3831·5	4054	4983
Calc.	...	3820	4072	4966
Diff.	...	+ 11·5	− 18	+ 17

Benzene. $[\alpha] = \frac{176{\cdot}0}{\lambda^2 - 0{\cdot}1363}$; $[M] = 5{\cdot}37\,[\alpha]$; $\lambda_0 = 0{\cdot}3692$.

Dextro	0·0905	+4540°	+4777°	+5877°
Laevo	0·0895	−4500	−4741	−5851
Mean (obs.)	...	4520	4759	5864
Calc.	...	4481	4779	5837
Diff.	...	+39·0	−20·0	+ 27·0

Pyridine. $[\alpha] = \frac{177{\cdot}3}{\lambda^2 - 0{\cdot}1354}$; $[M] = 5{\cdot}37\,[\alpha]$; $\lambda_0 = 0{\cdot}3680$.

Dextro	0·0912	+4560	+4770	+5887
Laevo	0·0898	−4515	−4726	−5860
Mean (obs.)	...	4537·5	4748	5873·5
Calc.	...	4494	4793	5853
Diff.	...	+ 43·5	− 45·0	+ 20·5

TABLE VII.

p-Iminocamphordiphenylamine.

Solvent.	Concentration-g./100 c.c.	Dextro, laevo, or mean.	[M] Na_D	[M] Hg_{yel}	[M] $Hg_{gr.}$
Ethyl alcohol	0·0306	*d*	+7107°	+7429°	+9275°
	0·0296	*l*	−7011	−7347	−9251
		Mean	7059	7388	9263
Pyridine	0·0301	*d*	+6726	+7000	+8818
	0·0308	*l*	−6736	−7006	−8837
		Mean	6731	7003	8827
Methyl alcohol	0·0303	*d*	+6303	+6518	+8236
	0·0306	*l*	−6237	−6454	−8189
		Mean	6270	6486	8213
Chloroform	0·0310	*d*	+5624	+5836	+7392
	0·0305	*l*	−5550	−5768	−7401
		Mean	5587	5802	7397
Acetone	0·0300	*d*	+5534	+5699	+7249
	0·0300	*l*	−5478	−5643	−7194
		Mean	5506	5671	7222
Benzene	0·0305	*d*	+5334	+5498	+7022
	0·0308	*l*	−5282	−5444	−6950
		Mean	5308	5471	6986

TABLE VIII.

Acetyl Derivative of p-Iminocamphordiphenylamine.

Benzene	0·1428	*d*	+2371°	+2462°	+3130°
	0·1400	*l*	−2364	−2471	−3152
		Mean	2368	2467	3141
Pyridine	0·1392	*d*	+2325	+2405	+3064
	0·1368	*l*	−2324	−2420	−3069
		Mean	2325	2413	3067
Chloroform	0·1424	*d*	+2220	+2301	+2929
	0·1444	*l*	−2202	−2293	−2900
		Mean	2211	2297	2915
Ethyl alcohol	0·1440	*d*	+2026	+2103	+2663
	0·1436	*l*	−2005	−2085	−2657
		Mean	2016	2094	2660
Acetone	0·1384	*d*	+2013	+2094	+2662
	0·1424	*l*	−1996	−2074	−2626
		Mean	2005	2084	2644
Methyl alcohol	0·1420	*d*	+1883	+1949	+2450
	0·1432	*l*	−1855	−1933	−2439
		Mean	1869	1941	2445

Table IX.

p-Aminocamphordiphenylamine.

Chloroform. $[\alpha] = \frac{18{\cdot}98}{\lambda^2 - 0{\cdot}0822}$; $[M] = 3{\cdot}34\,[\alpha]$; $\lambda_0 = 0{\cdot}2867$.

		Concentration : g./100 c.c.	[M] Na_D	$Hg_{yel.}$	$Hg_{gr.}$	$Hg_{vio.}$
Dextro	...	0·4068	+242·5°	+254·6°	+291·5°	+595·1°
Laevo	...	0·4024	−236·4	−253·1	−290·2	−585·1
Mean (obs.)	...	...	239·45	253.8	290·8	590·1
Calc.	...	...	239·1	251·6	293·5	588·4
Diff.	...	...	+0·35	+2·2	−2·7	+1·7

Acetone. $[\alpha] = \frac{16{\cdot}54}{\lambda^2 - 0{\cdot}0914}$; $[M] = 3{\cdot}34\,[\alpha]$; $\lambda_0 = 0{\cdot}3023$.

Dextro	...	0·4100	+215·9°	+232·1°	+264·7°	+566·1°
Laevo	..	0·4068	−209·3	−229·9	−262·6	−549·5
Mean (obs.)	...	...	212·6	231·0	263·65	558·8
Calc.	...	...	215·9	227·6	267·1	559·8
Diff.	...	...	−3·3	+3·4	−3·45	−1·0

Pyridine. $[\alpha] = \frac{10{\cdot}86}{\lambda^2 - 0{\cdot}085}$; $[M] = 3{\cdot}34\,[\alpha]$; $\lambda_0 = 0{\cdot}2915$.

Dextro	...	0·4024	+137·0°	+145·3°	+170·1°	+340·2°
Laevo	...	0·4060	−135·7	−147·9	−172·8	−349·7
Mean (obs.)	...	...	136·35	146·6	171·45	344·9
Calc.	...	...	138·2	145·5	170·0	345·6
Diff.	...	...	−1·85	+1·1	+1·45	−0·7

Methyl alcohol. $[\alpha] = \frac{14{\cdot}28}{\lambda^2 - 0{\cdot}0822}$; $[M] = 3{\cdot}34[\alpha]$; $\lambda_0 = 0{\cdot}2867$.

Dextro	...	0·4020	+182·8°	+195·2°	+220·2°	+440·2°
Laevo	...	0·4032	−174·0	−190·5	−215·4	−455·6
Mean (obs).	...	...	178·4	192·9	217·8	447·9
Calc.	...	...	179·9	189·3	220·7	442·9
Diff.	...	...	−1·5	+3·6	−2·9	+5·0

Ethyl alcohol. $[\alpha] = \frac{15{\cdot}94}{\lambda^2 - 0{\cdot}0799}$; $[M] = 3{\cdot}34[\alpha]$; $\lambda_0 = 0{\cdot}2827$.

Dextro	..	0·3988	+200·9°	+213·5°	+242·9°	+502·4°
Laevo	...	0·4008	−195·8	−212·5	−237·5	−484·3
Mean (obs).	...	...	198·35	213·0	240·2	493·35
Calc.	...	...	199·0	209·5	243·7	484·3
Diff	...	...	−0·65	+ 3·5	−3·5	+ 9·05

Benzene. $[\alpha] = \frac{19{\cdot}34}{\lambda^2 - 0{\cdot}0892}$; $[M] = 3{\cdot}34[\alpha]$; $\lambda_0 = 0{\cdot}2987$.

Dextro	...	0·4088	+253·3°	+269·6°	+306·4°	+661·8°
Laevo	...	0·4056	−247·4	−263·5	−305·4	−650·6
Mean (obs.)	...	...	250·35	266·55	305·9	656·2
Calc.	...	...	250·2	263·8	308·9	641·8
Diff.	...	...	+0·15	+2·75	−3·0	+14·4

TABLE X.

Diacetyl Derivative of p-*Aminocamphordiphenylamine.*

Chloroform. $[\alpha]=\frac{16{\cdot}81}{\lambda^2-0{\cdot}0761}$; $[M]=4{\cdot}18[\alpha]$; $\lambda_0=0{\cdot}2759$.

		Concentration : g./100 c.c.	[M] Na_D	$Hg_{yel.}$	$Hg_{gr.}$	$Hg_{vio.}$
Dextro	...	0·5000	+263·3°	+275·8°	+317·7°	+614·5°
Laevo	...	0·5020	−258·1	−274·8	−316·4	−608·0
Mean (obs.)	...	...	260·7	275·3	317·05	611·25
Calc.	...	...	259·6	272·9	316·8	614·9
Diff.	...	...	+1·1	+2·4	+0·25	−3·65

Benzene. $[\alpha]=\frac{17{\cdot}33}{\lambda^2-0{\cdot}0913}$; $[M]=4{\cdot}18\,[\alpha]$; $\lambda_0=0{\cdot}3022$.

Dextro	...	0·5020	+283·1°	+304·0°	+345·0°	+741·0°
Laevo	...	0·4996	−284·4	−301·2	−544·0	−736·2
Mean (obs.)	...	...	283·7	302·6	344·8	738·6
Calc.	...	...	283·0	298·4	350·0	734·7
Diff.	...	...	+0·7	+4·2	−5·2	+3·9

Acetone. $[\alpha]=\frac{15{\cdot}42}{\lambda^2-0{\cdot}0821}$; $[M]=4{\cdot}18[\alpha]$; $\lambda_0=0{\cdot}2865$.

Dextro	...	0·5040	+244·6°	+257·1°	+298·5°	+597·1°
Laevo	...	0·5004	−242·3	−259·0	−296·6	−593·2
Mean (obs.)	...	...	243·45	258·05	297·55	595·15
Calc.	...	...	243·1	255·8	298·4	598·1
Diff.	...	...	+0·35	+2·25	−0·85	−2·95
Pyridine.						
Dextro	...	0·5020	+124·9°	+137·4°	+166·5°	+337·3°
Laevo	...	0·5012	−125·1	−133·5	−162·7	−329·5
Mean	...	...	125·0	135·45	164·6	333·4

Rotations in the alcohols (ethyl and methyl) were not determined as the solubility in them was too small to determine the angle of rotation accurately.

TABLE XI.

pp'-Diphenylmethanebisiminocamphor.

Solvent.	Concentration : g./100 c.c.	Dextro laevo or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Pyridine	0·1248	*d*	+4552°	+4749°	+6016°
	0·1224	*l*	−4508	−4722	−6012
		Mean	4530	4736	6014
Benzene	0·1204	*d*	+4471	+4658·0	+5947
	0·1208	*l*	−4458	−4661	−5928
		Mean	4465	4660	5938
Chloroform	0·1240	*d*	+4442	+4620	+5873
	0·1204	*l*	−4410	−4615	−5846
		Mean	4426	4618	5860
Ethyl alcohol	0·1228	*d*	+4103	+4263	+5389
	0·1220	*l*	−4049	−4232	−5364
		Mean	4026	4248	5377

Acetone. $[\alpha]=\frac{157\cdot8}{\lambda^2-0\cdot1499}$; $[M]=4\cdot94[\alpha]$; $\lambda_0=0\cdot3871$.

Dextro	0·1196	+4005°	+4193°	+5285°
Laevo	0·1200	−3973	−4199	−5269
Mean (obs.)	...	3989	4196	5277
Calc.	...	3950	4234	5255
Diff.	...	+39	−38	+22

Methyl alcohol. $[\alpha]=\frac{161\cdot6}{\lambda^2-0\cdot1440}$; $[M]=4\cdot94[\alpha]$; $\lambda_0=0\cdot3795$.

Dextro	0·1244	+3990°	+4169°	+5220°
Laevo	0·1216	−3941	−4143	−5196
Mean (obs.)	...	3966	4156	5208
Calc.	...	3928	4201	5177
Diff.	...	+38	−45	+31

TABLE XII.

pp'-Diphenylmethanebisaminocamphor.

Solvent	Concentration : g./100 c.c.	Dextro, laevo or mean.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Benzene	0·4048	*d*	+486·0°	+529·0°	+602·9°
	0·3988	*l*	−493·2	−540·7	−605·6
		Mean	489·6	529·9	604·3
Chloroform	0·4036	*d*	+487·4	+530·3	+592·6
	0·4004	*l*	−485·1	−528·3	−591·2
		Mean	486·25	529·3	591·9
Pyridine	0·4040	*d*	+252·7	+283·5	+320·5
	0·4020	*l*	−247·8	−278·7	−315·9
		Mean	250·25	281·6	318·2

Methyl alcohol. $[\alpha]=\frac{17{\cdot}66}{\lambda^2-0{\cdot}0998}$; $[M]=4{\cdot}98[\alpha]$; $\lambda_0=0{\cdot}3159$.

Dextro	0·1980*	+352·2°	+377·3°	+440·1°
Laevo	0·1904*	−353·1	−379·2	−444·6
Mean (obs.)	...	352·7	378·25	442·35
Calc.	...	355·4	375·4	443·5
Diff.	...	−2·7	+2·85	−1·15

Acetone. $[\alpha]=\frac{26{\cdot}53}{\lambda^2-0{\cdot}0655}$; $[M]=4{\cdot}98[\alpha]$; $\lambda_0=0{\cdot}2559$.

Dextro	0·4000	+466·8°	+498·0°	+566·3°
Laevo	0·4048	−464·3	−502·0	−572·3
Mean (obs.)	...	465·55	500·0	569·3
Calc.	...	468·2	491·8	567·6
Diff.	...	−2·65	+ 8·2	− 1·7

* The solubility of the substance in methyl alcohol was found to be very small; hence half the usual concentration was employed in these experiments.

TABLE XII—*continued.*

Ethyl alcohol. $[\alpha] = \frac{23{\cdot}10}{\lambda^2 - 0{\cdot}0573}$; $[M] = 4{\cdot}98[\alpha]$; $\lambda_0 = 0{\cdot}2394$.

		Concentration : g./100 c.c.	[M] Na_D	[M] $Hg_{yel.}$	[M] $Hg_{gr.}$
Dextro	...	0·4020	+396·4°	+427·3°	+476·8°
Laevo	...	0·3968	−389·0	−420·5	−476·8
Mean (obs.)	...	...	392·7	423·9	476·8
Calc.	...	...	396·6	415·9	477·2
Diff.	...	...	−3·9	+8·0	−0·4

Further work on similar lines is in progress.

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Velocity of Esterification in Mixed Solvents.

By Balvant Wasudeo Bhide.

Previous experiments (Bhide and Watson, *J. Chem. Soc.*, 1927, p. 2102) have shown that if an inert solvent like benzene or ligroin is added to a solution of an organic acid in *iso*amyl alcohol with hydrogen chloride as catalyst, the rate of esterification is increased to many times its original value. As a probable explanation of these results it was suggested at the time that the reaction velocity depends more on the ratio of the concentration of the catalyst to the alcohol rather than on the concentration of the catalyst in the whole solution. If benzene is added to a solution of hydrogen chloride in *iso*amyl alcohol it is very likely that the hydrogen chloride molecules associate themselves with the alcohol molecules, as hydrogen chloride is only sparingly soluble in benzene. From calculations based on this hypothesis it was shown qualitatively that the velocity coefficients experimentally found showed a distinct similarity to those thus calculated.

The above hypothesis may be put to test by carrying out three series of experiments as follows.

(1) The catalyst is very soluble in *iso*amyl alcohol but sparingly soluble in the inert solvent.

(2) The catalyst is equally soluble in *iso*amyl alcohol and the inert solvent.

(3) The catalyst is sparingly soluble in *iso*amyl alcohol but very soluble in the inert solvent.

According to this hypothesis, in the first series of experiments the velocity coefficient ought to increase with increasing quantities of the inert solvent. The velocity coefficient-composition curve is hyperbolic. These experiments have already been carried out.

For the second series of experiments acetone was chosen as the inert solvent and phenylacetic acid as the organic acid. Hydrogen chloride is soluble to the same extent in acetone as in *iso*amyl alcohol. The substances were dried as usual. The results are given in Table I.

TABLE I.

Acetone per cent. ...	0	20	40	60	80	90
Velocity coefficient $\times 10^4$ ...	620	570	527	460	370	260

The velocity coefficients diminish with increasing quantities of acetone. As the acetone concentration increases the active alcohol-catalyst complexes diminish, and hence the fall in the velocity coefficients. It will be seen, however, that this rate does not decrease to the same extent as would be expected from solubility relations. Thus at 80 per cent. acetone concentration the velocity coefficient ought to be one-fourth of its original value, while actually it is only half. The discrepancy may be sought in the complex nature of the equilibria in such homogeneous solutions.

In the third series of experiments picric acid was chosen as the catalyst and benzene as the inert solvent, the organic acid and the temperature of experiment being the same as before. Picric acid is five times as much soluble in benzene as in *iso*amyl alcohol, the rate of esterification was slow. The percentage of ester formed in eight hours was measured. The results are given in Table II.

TABLE II.

Benzene per cent. ...	0	20	40	60	80
Ester per cent. ...	21	9	4	1	Nil.

The figures indicate sufficiently well the effect of benzene. At 80 per cent. benzene concentration the alcohol-catalyst complexes were so much diminished that the esterification was practically stopped.

It will be clear from the above experiments that the solubility of the catalyst in the neutral solvent is the predominant factor in determining the rate of reaction. In order to make these results more comprehensive, experiments were made to study the effect of neutral solvents on the decomposition of ethyl diazoacetate. Unfortunately hydrogen chloride does not act as a true catalyst for this reaction in *iso*amyl alcoholic solutions, ethyl chloroacetate being formed as the main product.

In the end I wish to thank the University of Bombay for a grant which defrayed the expenses of this work.

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Organo-Antimony Compounds. Part IV. Stibinic Acids derived from certain Local Anaesthetics.

By Sudhir Chandra Niyogy.

Of all the substances that have been put forward as a substitute for cocaine and its allied products for the production of local anaesthesia, the derivatives of aminobenzoic acid appear to be th e best. Cocaine, in spite of its intense local anaesthetic action, suffers from several disadvantages both chemical and commercial. In the first place cocaine induces "a habit" and secondly it has a distinctly injurious action on the heart. Moreover, the substance is costly and its preparation, even on a semi-commercial scale, has yet to be accomplished. The derivatives of aminobenzoic acids on the other hand do not suffer from any of these drawbacks.

Aminobenzoic acid is capable of elaboration in three directions:—

1. Esterification of the carboxyl group.
2. Substitution in the amino-group, with or without the elaboration of the ester grouping.
3. Substitution in the aromatic nucleus.

In the esterification of the carboxyl group, it has been found that the activity of the compound gradually increases up to amyl esters after which there is a falling off in the activity and that the introduction of an alkylamino-group in the alkyl ester group of aminobenzoic acid gives a compound possessing powerful local anaesthetic action.

When both the amino- and carboxyl groups of aminobenzoic acids are protected, a series of compounds are obtained of considerable activity. But the greatest drawback of this series of compounds is their insolubility in water, which however might be got over by the introduction of an acidic group.

The introduction of hydroxyl group into the nucleus of aminobenzoic acid gives a compound of about twice the anaesthetic activity but with an added antiseptic action. The simplest member

of the series is 3-oxy-4-aminobenzoic ester, whose toxicity is low and can therefore be used as a combined antiseptic and analgesic.

The next advance in this line was the fact discovered by Wichura (*Z. exp. Path. Ther.*, 7, 72) that the removal of the nuclear amino-group, does not, as might be expected, lead to the production of a compound of no local anaesthetic activity. In fact Wichura showed that benzoyl *N*-dimethylpropanol $C_6H_5COO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N(CH_3)_2$ has a moderate local anaesthetic activity and a very low toxicity, which makes it perfectly safe for use. It has been found in the course of this work that benzyl benzoate possesses the property of an excellent local anaesthetic. Its therapeutic index is sufficiently high to warrant its use for the production of local anaesthesia.

An attempt has been made to prepare the six possible isomeric nitro- and amino-derivatives of benzyl benzoate with a view to obtain the corresponding stibinic acid through the diazo-reaction. The object in view is to combine, in a stibinic acid, the aggregations of groups which can give rise to local anaesthesia so that it might be of use for the treatment of Kala-azar, by intramuscular injection, without any great local irritation. Although the physiological examination of these substances has not been as thorough as ought to be, owing to the absence of co-operation between the medical profession and research workers, yet it appears that these stibinic acids are almost without action for the treatment of Kala-azar, though they possess local anaesthetic action to a certain extent.

The first step in the process is the preparation of the six possible nitro-derivatives—three of them being derived from the three nitrobenzoic acids and the rest from the three nitrobenzyl alcohols. Of these, two only appear to have been studied by previous workers. Gomberg and Buchler (*J. Amer. Chem. Soc.*, 1920, **42**, 2059) has described the preparation of 2-nitrobenzyl benzoate and Bamberger and Renauld (*Ber.*, 1897, **30**, 2288), benzyl 4-nitrobenzoate. The method employed by Gomberg and Buchler is remarkable in some respects. 2-Nitrobenzyl chloride and sodium benzoate in water solution were heated to 115-20° for 8—10 hours. The solid that separated on cooling, gave the pure ester on crystallisation from dilute alcohol, as a *light brown* crystalline mass, m.p. 89-90°. It has been found that when the ester is prepared by the method of Gomberg and Buchler, the m.p. of the product is 89-90°, but when the ester is prepared by any other method, it melts at 101-2° and is a white

crystalline mass. This leads one to conclude that the product obtained by the previous authors was contaminated with colouring matters, which they did not attempt to remove, because it has been further observed that the reduction products of the nitro-bodies, by entirely different methods, gave the identical amine. But the most striking feature of the method of Gomberg and Buchler is that the reaction takes places smoothly in the case of the three nitrobenzyl chlorides and sodium benzoate but fails completely when nitrobenzoic acids (sodium salts) and benzyl chlorides are employed, though a greater part of benzyl chloride appears to undergo hydrolysis. This failure in the case of the substituted benzoic acids might be due to the hydrolysis of the esters produced during the first stage of the reaction, but it is strange that in no case, a trace of the ester was obtained, even when the temperature and the period of heating were varied.

Benzyl 4-nitrobenzoate has been prepared by Bamberger and Renauld (*Ber.*, 1897, **30**, 2288) by the action of 4-nitrobenzoyl chloride on benzyl alcohol. But as the preparation of 4-nitrobenzoyl chloride is a tedious operation, an easier and simpler method was considered to be necessary. The esterification of 4-nitrobenzoic acid was accomplished by simply heating an equimolecular quantity of the acid and benzyl alcohol to 160-80° for 4—5 hours. But attempts to prepare benzyl 3-nitrobenzoate by this method were unsuccessful. The usual method of the preparation of esters (by the action of dry hydrochloric or sulphuric acid upon the acid and alcohol) proved to be useless. On heating silver 3-nitrobenzoate and benzyl chloride in dry benzene suspension, no definite product was obtained. 3-Nitrobenzoyl chloride and benzyl alcohol, by the Schötten-Baumann reaction, gave the anhydride of 3-nitrobenzoic acid. Similar was the case with 2-nitrobenzoic acid, the silver salt of which was found to be soluble in water. As in the case of 4-nitro-benzoic acid, it was found that when an equimolecular quantity of 2-nitrobenzoic acid and benzyl alcohol was heated to 140-60° for 8—10 hours, the ester was formed in some cases but the results were not uniform, as in most cases an oil was obtained from which it was found impossible to separate the ester. The esterification of 2-nitro- and 3-nitro-benzoic acids was smoothly accomplished by allowing the corresponding acid chlorides in dry pyridine solution to react with the required quantity of benzyl alcohol also in dry pyridine, with cooling.

The reduction of these nitro-compounds to the corresponding amines was the next step in the process. The only known compound of this series is 2-aminobenzyl benzoate which has been described by Paul and Bodewig (*Ber.*, 1892, **25**, 2062). The reduction was carried out either with alcoholic ammonium sulphide or aluminium-mercury couple in moist ether solution (Morgan and Burgess. *J. Chem. Soc.*, 1921, **119**, 697). The isolation of the reduction product of 4-nitrobenzyl benzoate is extremely difficult.

The preparation of the corresponding stibinic acids from these amino-esters necessitated particular care to prevent the hydrolysis of the ester grouping during the alkaline decomposition of the diazo-compound. An English Patent (313,058 of 1928) describes the preparation of aryl stibinic acids by a method, which, if successful, will render the preparation of these acids far less difficult and tedious. According to this patent, the additive compound obtained by treating a diazotised solution of amine in hydrochloric acid and antimony trichloride is dried and added to pyridine in small quantities at a time. On standing at ordinary temperature or warming on a water-bath between 60° and 70°, nitrogen is given off smoothly and on diluting with water, the aryl-stibinic acid is precipitated. But when attempts were made to prepare the stibinic acid from the amino-esters described in this communication by the above process, the products were not the expected compound but a brown resinous mass, completely insoluble in alkali, but which was found to contain antimony. The products were insoluble in all organic solvents including pyridine and could not be further purified.

Experimental.

Benzyl 2-Nitrobenzoate.—2-Nitrobenzoic acid (10 g.) and redistilled thionyl chloride (50 g.) were heated on a water-bath under reflux for 2 hours. The excess of thionyl chloride was then removed by heating under *vacuo* on a boiling water-bath. The residue in the flask was allowed to cool and then dissolved in pyridine (20 c.c.) which had previously been dried over anhydrous sodium carbonate. To a solution of benzyl alcohol (5·6 c.c.) in dry pyridine (10 c.c.) and cooled in ice, the acid chloride was added in small quantities at a time and thoroughly mixed after each addition. The reaction mixture became warm after each addition and was cooled in ice before

further addition was made. During the first stages of the reaction a yellowish-white solid separated which increased as more acid chloride was added, till after the addition of the whole the mixture became almost solid. The reaction vessel was then allowed to stand overnight in ice and then heated on a water-bath for 2 hours under reflux to complete the reaction. The hot liquid was then poured into crushed ice when a yellow oil separated which solidified after sometime. It crystallised from dilute methyl alcohol in glistening white plates, m.p. 54-55° (yield, 13 g.). (Found: N, 5·56. $C_{14}H_{11}O_4N$ requires N, 5·44 per cent.).

Benzyl 3-Nitrobenzoate.—The ester was prepared from 3-nitrobenzoic acid and thionyl chloride as described before. But the isolation of the ester was far more difficult.

When the hot pyridine solution, after the completion of the reaction, was poured into crushed ice, a thick yellow oil separated, which did not solidify even when cooled in a freezing mixture. On allowing to stand in a refrigerator overnight, a semi-solid mass was obtained. This was rapidly filtered off, dissolved in methyl alcohol, boiled with animal charcoal and filtered. The filtrate on cooling in a freezing mixture did not give any precipitate. On dilution, however, a light yellow oil was obtained, which on prolonged standing in a freezing mixture and scratching with a glass rod, solidified to a pale yellow solid. This was collected, washed with water and then with dilute sodium carbonate and again with water and then dried on a porous plate. The crystallisation of the compound was effected by dissolving it in methyl alcohol and then diluting with a small quantity of water when a yellow oil separated. The oil was then dissolved by warming the liquid and adding a small quantity of methyl alcohol. On cooling the solution in ice, the ester separated as white needles, m.p. 48-49° (yield, 12 g. from 10 g. of 3-nitrobenzoic acid). (Found: N, 5·67. $C_{14}H_{11}O_4N$ requires N, 5·44 per cent.).

Benzyl 4-Nitrobenzoate.—4-Nitrobenzoic acid (16·7 g.) and benzyl alcohol (10·8 c.c.) were heated on an oil-bath for 10 hours between 160° and 180°. On cooling the contents of the vessel solidified. The whole was taken up with rectified spirit, boiled with animal charcoal and filtered. The filtrate on cooling somewhat, deposited a certain quantity of a solid which was found to be a mixture of 4-nitrobenzoic acid and the required ester. This was filtered off and on diluting the filtrate the ester separated as white needles, m.p. 83-84° (yield, 25 g.).

2-*Nitrobenzyl Benzoate*.—This compound when prepared according the method of Gomberg and Buchler (*loc. cit.*) was a light brown crystalline mass, m.p.89-90°. But when prepared by the following method the m.p. was 101-2°.

2-Nitrobenzaldehyde (20 g.) was gradually added to a solution of caustic potash (10 g.) in water (60 c.c.) with cooling in ice and vigorous agitation after each addition of the aldehyde. It was found that the whole of the nitroaldehyde did not go into solution. The mixture was then allowed to stand for 3 days when a large quantity of needle-shaped crystals was found to have separated. The contents were then diluted with water (100 c.c.) when the solid dissolved. The alkaline liquid was then extracted thrice with ether, the ethereal layer separated and dried over ignited sodium sulphate overnight. On removing the ether, a light yellow liquid (2-nitrobenzyl alcohol) was left.

2-Nitrobenzyl alcohol was then condensed with benzoyl chloride in pyridine solution as described under the preparation of benzyl 2-nitrobenzoate. The crude product melted at 89-95°, but when twice recrystallised from absolute alcohol the m.p. rose to 101-2°. (Found: N, 5·57. $C_{14}H_{11}O_4N$ requires N, 5·44 per cent.).

3-*Nitrobenzyl Benzoate*.—3-Nitrobenzyl alcohol was prepared from 3-nitrobenzaldehyde as described above. The oil left after the evaporation of ether was dried by heating under vacuum on a boiling water-bath for 2 hours and left overnight. Phosphorus pentachloride (10 g.) was then gradually added to the dried oil in small portions. The reaction was very vigorous during the first stage but slackened off towards the end. Phosphorus oxychloride was then distilled off from a water-bath under reduced pressure. The residual oil, 3-nitrobenzyl chloride, amounted to 7 g.

The reaction between 3-nitrobenzyl chloride and sodium benzoate was carried out according to the method of Gomberg and Buchler (*loc. cit.*). To a solution of sodium benzoate (10 g. in 50 c.c. of water), 3-nitrobenzyl chloride (7 g.) was added and the mixture heated under reflux for 9 hours. On cooling a yellowish-white solid separated. This was filtered off and twice recrystallised from alcohol, m.p. 71-72° (yield, 8 g.). (Found: N, 5·64. $C_{14}H_{11}O_4N$ requires N, 5·44 per cent.).

4-*Nitrobenzyl benzoate* was similarly obtained from 4-nitrobenzyl chloride and sodium benzoate. The crude product was

crystallised from alcohol in light red prisms, m.p. 94-95°. (Found: N, 5·56. $C_{14}H_{11}O_4N$ requires N, 5·44 per cent.).

3-*Nitrobenzoic Anhydride*.—3-Nitrobenzoic acid (11 g.) was gradually mixed with phosphorus pentachloride (14 g.). After the first addition of the pentachloride the flask was slightly warmed but during the latter stages vigorous evolution of hydrochloric acid showed that the reaction was proceeding rapidly. Phosphorus oxychloride was then removed under reduced pressure (yield, 14 g.).

Benzyl alcohol (5·5 c.c.) was then added to the chloride prepared and cooled in ice. Caustic soda solution (10%) was then gradually added to the mixture of the alcohol and acid chloride, with violent agitation, till alkaline. A pasty mass was obtained which was filtered off, dried on a porous plate and then crystallised from benzene in yellowish-white, glistening plates, m.p. 162°—63°. (Found: C, 52·48; H, 2·8; N, 8·9. $C_{14}H_8O_7N_2$ requires C, 53·16; H, 2·6; N, 8·86 per cent.).

2-*Nitrobenzoic Anhydride*.—The preparation of the compound was carried out similarly employing thionyl chloride instead of phosphorus pentchloride. The solid product was crystallised from benzene in white needles, m.p. 128°-29°. (Found: N, 9·18. $C_{14}H_8O_7N_2$ requires N, 8·86 per cent.).

Benzyl 4-Aminobenzoate.

Benzyl 4-nitrobenzoate (10 g.) was dissolved in alcohol with warming, the solution cooled and saturated with dry ammonia gas for 1 hour. A slow steam of sulphuretted hydrogen was then passed through the solution for 4 hours which was then evaporated to dryness on a water-bath. The residue was taken up in alcohol and boiled for 2 hours under reflux with the addition of copper powder to remove sulphur. Copper sulphide was then filtered off and on diluting the filtrate a white crystalline solid separated. This was dried on a porous plate, dissolved in benzene and precipitated by the addition of a large excess of petroleum ether, filtered and dried in *vacuo* over liquid paraffin; m.p. 90—91°. (yield, 5·6 g.). (Found: N, 6·54. $C_{14}H_{13}O_2N$ requires N, 6·16 per cent.).

Benzyl 3-Aminobenzoate.—The nitro-compound was dissolved in alcohol and the reduction was carried out as described above. The residue obtained by evaporating the alcoholic liquid was repeatedly extracted with cold dilute hydrochloric acid, neutralised with dry

sodium carbonate, when a white emulsion was obtained. The whole was then extracted with ether, the ethereal layer dried over ignited sodium sulphate, and then evaporated to dryness. A yellow oily liquid remained which when treated with a few drops of dilute hydrochloric acid solidified. The solid was dissolved in alcohol and precipitated by the addition of a large excess of benzene, as white needles, m.p. 199-200°. (Found: N, 5·65. $C_{14}H_{14}O_2NCl$ requires N, 5·35 per cent.).

The substance is soluble in water, gives diazo-reaction and, with silver nitrate, a white precipitate of silver chloride. An alcoholic solution of the substance is distinctly acidic in reaction. All these show that the substance is the hydrochloride of benzyl 3-aminobenzoate.

Benzyl 2-Aminobenzoate.

The nitro-compound (5 g.) was dissolved in moist ether and treated with aluminium—mercury couple prepared from aluminium foil (3 g.) during 4 hours. During the progress of the reaction, the ether solution which was colourless at first, gradually assumed a pink colour. The reaction flask was then allowed to stand overnight, the sludge filtered off, washed with ether and dried over sodium sulphate. The dried ether solution was then treated with slow stream of dry hydrochloric acid, when a white solid separated. This was rapidly dried on a porous plate, dissolved in chloroform and precipitated with petroleum ether, as white needles m.p. 162-63° (yield, 2·5 g.). (Found: N, 4·98. $C_{14}H_{14}O_2NCl$ requires N, 5·35 per cent.).

The properties of the compound (*cf.* above) show that the substance is not the free base but the hydrochloride.

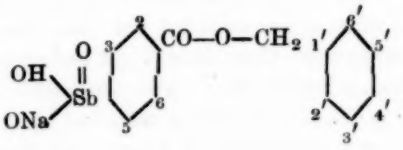
2-Aminobenzyl Benzoate.—Attempts to prepare this compound according to the method of Paul and Bodewig (*loc. cit.*) were unsuccessful. The reduction was carried out as described for benzyl 2-nitrobenzoate. The crude product was crystallised by dissolving in chloroform and precipitating with petroleum ether. The product thus obtained had an m.p. 144-45°, identical with that described by Paul and Bodewig (*loc. cit.*).

3-Aminobenzyl benzoate was obtained from 3-nitrobenzyl benzoate in moist ether with aluminium—mercury couple. The reduction product was isolated by passing hydrochloric acid through the ether

solution. The crystallisation was effected by dissolving in alcohol and precipitating with ether, m.p. 198-99°. (Found: N, 5·4. $C_{14}H_{14}O_2NCl$ requires N, 5·35 per cent.).

The reduction of 4-nitrobenzyl benzoate was first carried out with hydrogen sulphide in ammoniacal alcoholic solution and the yellow liquid obtained after the removal of sulphur and evaporation of the solvent (alcohol) was left overnight in a vacuum desiccator. It was found that the yellow oil had been converted into a dark brown resinous mass which is insoluble in alcohol and fails to respond to the usual tests of amine. In moist ether solution, with aluminium—mercury couple, the nitro-body was smoothly converted into the amine but the isolation of the product proved to be futile. The oil that was obtained after evaporation of ether, decomposed into resinous mass as described before. On attempting to isolate the base as its hydrochloride from the ether solution (which was dried overnight over anhydrous sodium sulphate) by passing a current of dry hydrochloric acid gas, a white solid separated at first but it rapidly turned brown. This change of colour was so rapid that it was found impossible to prevent it. Attempts to isolate the hydrochloride from the brown mass were unsuccessful.

Preparation of Benzyl Benzoate-4-stibinate of Sodium.



Benzyl 4-aminobenzoate (4·4 g.) was added to well-cooled dilute hydrochloric acid (5 c.c. conc. acid. in 40 c.c. water) cooled in a freezing mixture and diazotised with sodium nitrite (1·5 g.). It was found that the whole of amine did not go into solution, though the solution was found to contain an excess of nitrous acid. The liquid was then rapidly filtered through a cold filter and the clear filtrate treated with a further quantity of cooled dilute hydrochloric acid (5 c.c.). Antimony trichloride prepared by dissolving antimony

trioxide (2 g.) in hydrochloric acid (15 c.c.) was added to the diazo-solution when a yellow precipitate separated. This was filtered off and a portion was dried on a porous plate.

The main portion was suspended in water, cooled to 5° and a dilute solution of caustic soda (5%) was added with vigorous agitation till faintly alkaline. During the addition, the temperature of the liquid was always kept below 10°. After the evolution of nitrogen had slackened off, the liquid was filtered off and the clear filtrate acidified with dilute sulphuric acid when the stibinic acid separated as a light brown gelatinous mass. This was allowed to settle and then filtered and washed free from sulphuric acid as far as possible. The mass was then suspended in water and dilute caustic soda solution added drop by drop till neutral and the solution evaporated to dryness in vacuum over sulphuric acid. The brown residue was then extracted with methyl alcohol, filtered and the filtrate treated with an excess of the ether when the sodium salt of the stibinic acid separated as a light yellow precipitate. This was filtered off, washed repeatedly with ether and then dried in *vacuo* over liquid paraffin. (Found: Sb, 30·7. $C_{14}H_{12}O_5SbNa$ requires Sb, 31·35 per cent.).

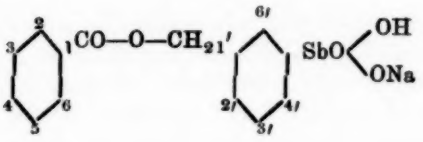
The portion of the additive product which had been dried on the porous plate was added to pyridine (25 c.c.) in small portions at a time. The colour of the pyridine changed first to yellow and then to red during the course of the addition and nitrogen was also given off. After the addition was complete, the liquid was warmed on a water-bath between 60° and 70° till the evolution of gas ceased. It was found that the whole of the solid did not pass into solution. The insoluble impurities were then filtered off and on diluting the clear pyridine solution, a brown pasty mass separated which was found to be insoluble in alkali. The brown mass was again dissolved in pyridine, heated on a water-bath for ½ hour and then diluted: a brownish solid separated which was found to certain antimony but which was completely insoluble in dilute alkali and cannot be the expected stibinic acid. As further purification of the product was not possible, its identity could not be determined.

Benzyl benzoate-3-stibinate of sodium was obtained from the hydrochloride of benzyl 3-aminobenzoate, by the method already described. (Found: Sb, 30·34. $C_{14}H_{12}O_5SbNa$ requires Sb, 31·33 per cent.).

Benzyl Benzoate-2-stibinate of Sodium.

This was prepared from the hydrochloride of benzyl 2-amino-benzoate. (Found: Sb, 30·1. $C_{14}H_{12}O_5SbNa$ requires Sb, 31·33 per cent.).

Benzyl Benzoate-5′-stibinate of Sodium.



(Found: Sb, 30·58. $C_{14}H_{12}O_5SbNa$ requires Sb, 31·33 per cent.).

My thanks are due to Prof. H. K. Sen for the interest he has taken in this work, without which it would have been difficult for me to finish this work.

Department of Applied Chemistry,
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Calcutta.

Received May 7, 1930.

Note on an Electrolytic Method of Preparing Silver Oxide.

By M. Raman Nayar and P. S. MacMahon.

While conducting experiments on Kohlschütter's (*Z. Elektrochem.*, 1908, **14**, 49) method of preparing silver hydrosol it was felt that silver oxide prepared chemically by precipitation of silver nitrate with sodium hydroxide was possibly contaminated by adsorbed impurities not easily removable by washing. An unobjectionable method of preparing the oxide free from all electrolytes was desirable, especially in view of the theory advanced by Pauli and co-workers, that a small amount of electrolyte is necessary for the preparation of silver hydrosol.

Such a method is furnished by conducting the electrolysis between silver electrodes in conductivity water as in Bredig's preparation of silver hydrosols. We have been using this method since 1925 for the preparation of silver oxide free from all electrolytes (*Proc. Indian Soc. Congress, Lahore*, 1927, p. 171.). The oxidation of silver anode under such conditions was first noticed by Morse (*Proc. Amer. Acad.*, 1910). Recently a paper has also appeared by Best and Cox (*J. Chem. Soc.*, 1929, p. 2727) who found that the electrolyte produced in the Bredig method of sparking is essentially silver hydroxide. But we do not know of any one having employed this method for preparation of silver oxide.

Pure silver electrodes are dipped in conductivity water $K = 1{\cdot}2 \times 10^{-6}$ in a silica beaker and an arc struck for a minute or two, when enough silver oxide is produced to make the water fairly conducting; the electrodes are then separated 2–3 mm. and electrolysis continued. With 220 volts the current rises nearly to 1 amp. in a few minutes. The anode gets deposited with a dark brown coating of oxide and the cathode with grey spongy silver. No peroxide was detected. Shining films of silver float on the surface of the liquid and tiny sparks are often produced on the surface of films. The liquid gets heated and may even be boiling. The products can be easily scraped from the electrode by a rod of silica or silver and fall to the bottom of the

vessel. The substance is not pure silver oxide but a mixture of silver oxide and silver of varying composition. Under the ordinary conditions obtaining in preparation of Bredig's silver sol the analysis of the products gave the following results in two samples: –

	I.	II.
Ag_2O	61·66 per cent.	57·69 per cent.
Ag	38·34 per cent.	42·31 per cent.

As previously stated this product is free from all contamination of electrolytes which may be expected in the chemical method of preparation.

Department of Chemistry,
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Received March 17, 1930.

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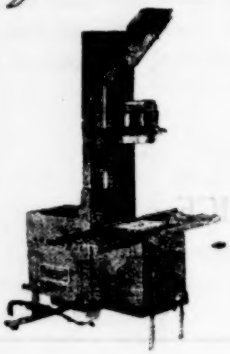

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Preparation and Study of some Hydroxide Jellies.

By Satya Prakash and N. R. Dhar.

In a previous communication (*Z. anorg. Chem.*, 1927, **168**, 214) it was reported that hydroxide jellies of iron, chromium and aluminium can be obtained by treating their metallic chlorides or nitrates with sodium acetate in presence of a small amount of ammonium sulphate and ammonia. In this paper, we have investigated in detail the conditions of formation of the following jellies:—Ferric hydroxide, chromium hydroxide, aluminium hydroxide, stannic hydroxide and zirconium hydroxide.

Ferric Hydroxide Jellies.

For the preparation of this jelly, we started with *M*/2-ferric chloride solution in test tubes and added varying amounts of sodium acetate solution to it. To the red solution thus obtained was added a little of ammonium sulphate solution. A small quantity of ammonia was also added and the mixture, which was acidic, was shaken and allowed to stand for some time. It soon develops opalescence and finally, a gelatinous precipitate or a jelly is obtained according to the concentrations of the various reacting constituents. Thus the jelly is obtained in an acid medium.

The influence of the variation of the concentrations of sodium acetate, ammonium sulphate, ammonia and ferric chloride has been studied in the following tables:

Ferric chloride solution	*M*/2.
Sodium acetate solution	3·54*N*.
Ammonium sulphate	2*M*.
Ammonia	5·81*N*.

TABLE I.

Variation of Sodium Acetate.

To 2 c. c. of ferric chloride solution were added 0·5 c. c. of ammonium sulphate and 0·1 c. c. of ammonia and varying concentrations of sodium acetate. The total volume was made up to 5 c. c. in each case by adding the requisite amount of water.

Sodium acetate.	Observation.
0·8 c. c.	Clear solution, no jelly.
0·9	,, ,,
1·0	Turbid solution, no jelly.
1·1	Turbid viscous solution.
1·2	Set to loose jelly in 20 hrs.
1·3	Set to firm opaque jelly in 20 hrs.
1·4	,, ,, ,,
·5	Opaque solution, but no jelly.

TABLE II.

Variation of Ammonium Sulphate.

Ferric chloride solution = 2 c. c. Sodium acetate = 1·2 c. c.
Ammonia = 0·1 c. c. Total volume = 5 c. c.

Ammonium sulphate.	Observation.
0·2 c. c.	Set to loose opaque jelly within 22 hrs.
0·4	,, firm ,, ,, ,,
0·6	,, ,, ,, ,, 15 ,,
0·8	,, ,, ,, ,, 10 ,,
1·0	,, loose jelly within 22 hrs.

TABLE III.

Variation of Ammonia.

Ferric chloride solution = 2 c. c. Sodium acetate = 1·2 c. c.
Ammonium sulphate = 0·6 c. c. Total volume = 5 c. c.

Ammonia.	Observation.
0 c. c.	Clear solution, no jelly.
0·1	Set to opaque firm jelly in 22 hrs.
0·2	,, ,, within 22 hrs.
0·3	,, loose jelly ,, ,,

TABLE IV.

Variation of Ferric Chloride.

Total volume = 5 c. c.

Ferric chloride :.	Sodium acetate.	Ammonium sulphate.	Ammonia.	Observation.
1 c. c.	1·0 c. c.	0·2 c. c.	0·1 c. c.	No jelly, precipitate.
1	1·2	0·5	,,	,,
1·33	1·0	0·2	,,	Opaque loose jelly in 22 hrs.
,,	0·8	,,	,,	,, firm ,, ,,
,,	1·0	,,	0	,, ,, ,, ,,
2·0	1·2	,,	0·1	,, ,, ,, ,,

From the results recorded in these tables, it will be seen that for a given amount of ferric chloride, there is a corresponding minimum amount of sodium acetate which must be added before a jelly is expected. A small quantity above this minimum is always favourable, but the addition of larger amounts of sodium acetate will not form the jelly. As regards the addition of ammonium sulphate, a small quantity is always sufficient ; the addition of it beyond a limit gives loose jellies or gelatinous precipitates. The addition of a trace of ammonia is sufficient to give a jelly if the concentrations of other constituents are suitable. In some jellies with higher concentrations of ferric chloride, it has been observed that the addition of ammonia is not essential, but if a trace of it is added, the jelly is more easily formed. The jellies of ferric hydroxide obtained by this method are opaque and stable, and do not undergo any marked syneresis and some of them can be preserved for months.

Chromium Hydroxide Jellies.

Our method of preparation of this jelly consists in taking a known amount of chromic chloride solution in test tubes and then adding a sufficient amount of sodium acetate to it. The mixture is allowed to stand for an hour and then some amount of ammonia and then a little of ammonium sulphate are added to it. If the mixture is not allowed to stand for sufficient time before the addition of ammonia, precipitation occurs and no jelly is obtained. The clear

mixture obtained in the way described develops opalescence and finally translucent or opaque violet jellies of fine texture are obtained.

Chromic chloride solution	*M*/2.
Sodium acetate	3·54*N*.
Ammonium sulphate	2*M*.
Ammonia	5·81*N*.

TABLE V.

Variation of Sodium Acetate.

Chromic chloride solution = 2 c. c. Ammonium sulphate = 0·5 c. c.
Total volume = 5 c. c.

Sodium acetate.	Ammonia.	Observation.
0·7 c. c.	0·7 c. c.	No jelly, slight precipitate.
1·0	,,	Translucent violet jelly in 2 hrs. 45 mins.
1·3	,,	,, ,, 1½ hrs.
1·5	,,	Clear solution, no jelly.
,,	1·0	Firm opaque jelly in 2 hrs.
,,	0·5	No jelly, clear solution.

TABLE VI.

Variation of Ammonium Sulphate.

Chromic chloride solution = 2 c. c. Sodium acetate = 1·3 c. c.
Ammonia = 0·7 c. c. Total volume = 5 c. c.

Ammonium sulphate.	Observation.
0·2 c. c.	Firm translucent jelly in 1 hr.
0·5	,, ,, 1½ hrs.
0·7	Firm opaque jelly in 2 hrs.
1·0	,, ,, 2 hrs. 45 mins.

TABLE VII.

Variation of Ammonia.

Chromic chloride solution = 2 c. c. Total volume = 5 c. c.

Sodium acetate.	Ammonium sulphate.	Ammonia.	Observation.
1·5 c. c.	0·5 c. c.	0·5 c. c	No jelly, clear solution.
,,	,,	0·7	,, ,, ,,
,,	,,	1·0	Firm jelly in 2 hrs.
1·0	,,	0·5	No jelly, clear solution.
,,	,,	0·7	Translucent jelly in 2 hrs. 45 mins.
,,	,,	1·0	,, ,, 15 hrs.
,,	,,	1·3	Opaque jelly in 2½ hrs.
,,	1·0	1·0	,, ,, 15 hrs.

TABLE VIII.

Variation of Chromic Chloride.

Ammonium sulphate = 0·5 c.c. Total volume = 5 c. c.

Chromic chloride.	Sodium acetate.	Ammonia.	Observation.
2 c. c.	1 c. c.	0·7 c. c.	Translucent jelly in 2 hrs. 45 mins.
1	1	,,	Opaque jelly in 22 hrs.
0·5	1	,,	Loose jelly in 1 day.
2	1	0·5	No jelly, clear solution.
1	1	,,	Translucent jelly in 4½ hrs.
0·5	1	,,	Loose jelly in 1 day.
,,	1·5	1·0	Opalescent solution, no jelly.

Just as in the case of ferric hydroxide jellies, in this case also, a minimum amount of sodium acetate is fixed for a given amount of chromic chloride for jelly formation. Similarly, the addition of greater quantities of ammonium sulphate always gives jellies of weaker texture in a longer time. The regulation of the quantity of ammonia is an important factor in the formation of this

jelly, and a sufficient amount of ammonia has always to be added before a jelly could be expected. The addition of ammonia above a fixed minimum always diminishes the time of setting. The jellies obtained with dilute solutions of chromic chloride are translucent and those with concentrated solutions are opaque. The jellies are stable and of fine texture and do not undergo any marked syneresis.

Aluminium Hydroxide Jellies.

In our method of preparation of this jelly, a known amount of aluminium nitrate solution is taken in test tubes and varying concentrations of sodium acetate and ammonium sulphate are added to it. To the mixture is then added the requisite amount of ammonia, drop by drop with constant stirring; and thus a clear colourless solution is obtained which soon develops opalescence on standing, and if the cencentrations are favourable, firm translucent or opaque jellies are obtained. These jellies are stable and quite uniform in texture. The influence of the variation of concentrations of different constituents is recorded in the following tables:—

Aluminium nitrate	*M*/2.
Sodium acetate	3·54 *N*.
Ammonium sulphate	2*M*.
Ammonia	5·81 *N*.

TABLE IX.

Variation of Sodium Acetate.

Aluminium nitrate solution = 2 c.c. Ammonia = 0·5 c.c.
Total volume = 5 c.c.

Sodium. acetate.	Ammonium sulphate.	Observation.
1 c.c.	0·5 c.c.	Transparent jelly in 3 days.
1	0 7	Translucent jelly within 22 hrs.
1·2	0·7	Precipitate, no jelly.
1·5	0·7	Precipitate, no jelly.
1·8	0·7	Precipitate, no jelly.

TABLE X.

Variation of Ammonium Sulphate.

Aluminium nitrate solution = 2 c.c. Sodium acetate = 1 c.c.
Ammonia = 0·5 c.c. Total volume = 5 c.c.

Ammonium sulphate.	Observation.
0·5 c.c.	Transparent jelly in 3 days.
0·7	Translucent jelly in 22 hrs.
1·0	,, ,, ,,
1·2	Opaque jelly within 22 hrs.
1·5	,, ,, ,,

TABLE XI.

Variation of Ammonia.

Aluminium nitrate solution = 2 c.c. Sodium acetate = 1 c.c.
Total volume = 5 c.c.

Ammonium sulphate.	Ammonia.	Observation.
0·5 c.c.	0·5 c.c.	Transparent jelly in 3 days.
0·5	0·6	Translucent jelly in 27 hrs.
0·5	0·7	White precipitate, no jelly.
0·5	0·8	,, ,, ,,
0·7	0·3	Transparent jelly in 3 days.
0·7	0·4	Translucent jelly in 26 hrs.
0·7	0·5	Translucent jelly within 22 hrs.
0·7	0·6	,, ,, ,,

TABLE XII.

Variation of Aluminium Nitrate.

Total volume = 5 c.c.

Aluminium nitrate.	Sodium acetate.	Ammonium sulphate.	Ammonia	Observation.
2 c.c. of 0·5*M*	1·0 c.c.	0·7 c.c.	0·5 c.c.	Translucent jelly in 22 hrs.
2 of 0·75*M*	1·1	6·7	0·5	Translucent jelly in 2 days.
2 ,,	1·1	0·2	0·5	,, ,, ,,
2 ,,	1·1	0·9	0·5	,, ,, ,,
2 ,,	1·1	0·7	0·6	Precipitate, no jelly.
1 of 0·5*M*	1·0	0·7	0·5	No jelly.

Firm transparent or translucent jellies are obtained by this method. In some cases, the opalescence increases with time and finally, the jellies become opaque. There appears to be a very limited range over which the quantity of sodium acetate could be varied. The addition of large amounts of ammonium sulphate slightly decreases the time of setting, but increases the opacity of the jelly.

The greater the concentration of ammonium sulphate, the less will be the amount of ammonia to give a jelly. The regulation of the quantity of ammonia is also an important factor, for which a minimum concentration is necessary, but the addition of it in amounts greater than the minimum gives either opaque loose jellies or precipitates.

Stannic Hydroxide Jellies.

Weiser (*J. Phys. Chem.*, 1922, **26**, 654) claims to have obtained transparent jellies of stannic hydroxide by coagulating a sol of stannic oxide prepared by Zsigmondy's method. Our method for the preparation of iron, chromium, and aluminium jellies can be extended to obtain stannic hydroxide jellies. The jellies obtained by this method are mostly opaque, but some are translucent at the time of formation but become opaque on standing. Some of the jellies have a tendency to synerise. *M*/2-Solution of tin tetrachloride (liquid, Kahlbaum) was taken in test tubes, and to it varying concentrations of sodium acetate and a little of ammonium sulphate were added. The solution soon dovelops opalescence and finally a jelly is obtained. The addition of ammonia is not necessary to obtain this jelly, but in certain cases, specially when the solution is obtained by dissolving hydrated crystals of stannic chloride which always contain free hydrochloric acid, the addition of ammonia is essential to obtain a jelly.

Stannic chloride	*M*/2.
Sodium acetate	3·54*N*.
Ammonium sulphate	2 *M*.
Ammonia	5·81*N*.

TABLE XIII.

Variation of Sodium Acetate.

Stannic chloride solution = 2 c.c. Ammonium sulphate = 0·5 c.c.
No ammonia was added. Total volume = 5 c.c.

Sodium acetate.	Observation.
0·5 c.c.	Clear solution, no jelly.
0·7	Clear solution, no jelly.
0·9	Opaque jelly in 1 day.
1·0	Opaque jelly in 1 day, slight syneresis after 2 days.
1·2	Immediately opaque jelly, readily undergoing syneresis.

TABLE XIV.

Variation of Ammonium Sulphate.

Stannic chloride solution = 2 c.c. Sodium acetate = 1 c.c.
No ammonia was added Total volume = 5 c.c.

Ammonium sulphate.	Observation.
0·5 c. c.	Opaque jelly in 1 day.
0·6	Opaque jelly in 14 minutes, syneresis starting after 5 hrs.
0·7	Opaque jelly in 10 minutes, syneresis soon starts.
0·9	Opaque jelly in 2 minutes, syneresis soon starts and the jelly breaks up in a day.

TABLE XV.

Variation of Ammonia.

Stannic chloride solution = 2 c.c. Sodium acetate = 0·7 c.c.
Ammonium sulphate = 0·5 c.c. Total volume = 5 c.c.

Ammonia.	Observation.
0 c. c.	Clear solution, no jelly.
0·1	White opaque jelly in 32 hrs.
0·2	White opaque jelly in 22 hrs.
0·3	Loose jelly immediately, which soon breaks up.
0·4	" " " "

TABLE XVI.

Variation of Stannic Chloride.

No ammonia was added. Total volume = 5 c. c.

Stannic chloride.	Sodium acetate.	Ammonium sulphate.	Observation.
1 c. c.	0·5 c c.	0·5 c. c.	Precipitate, but no jelly.
1	0·5	0·1	Opaque jelly in 10 min., undergoing syneresis in 1 day.
2	0·5	0·1	No jelly.
1	0·4	0·1	Firm opaque jelly in 1 day, slight syneresis after 2 days.
2	0·4	0·1	No jelly.

It will be seen from these tables that there is a limited range of sodium acetate which will produce a jelly. The jellies obtained by the addition of large amounts of either sodium acetate or ammonium sulphate begin to synerise at once. The addition of ammonia appears to be favourable where the concentrations of sodium acetate and ammonium sulphate are insufficient to give jellies.

Zirconium Hydroxide Jellies.

We have observed that opaque white jellies of zirconium hydroxide are obtained by simply adding the solution of sodium acetate to zirconium nitrate solution, and allowing the mixture to stand for some time. The addition of potassium or ammonium sulphate is not essential though favourable for the jelly formation. Like stannic hydroxide jellies, the addition of ammonia is not required. The jellies obtained by this method are opaque or translucent at the time of setting, but become opaque on standing. Some of the jellies are stable while others melt, break or synerise after a time.

TABLE XVII.

Total volume = 5 c. c.

Zirconium-nitrate ($M/2$).	Sodium-acetate ($3{\cdot}54$-N).	Observation.
1 c. c.	0·2 c. c.	Clear solution, no jelly.
1	0·3	Clear solution, no jelly.
1	0·5	Translucent jelly in 2½ min., not synerising in 1 day.
1	0·7	Translucent jelly in 1½ min., not synerising in 1 day.
2	0·3	Clear solution, no jelly.
2	0·4	,, ,, ,,
2	0·45	,, ,, ,,
2	0·5	Translucent jelly in 4 min., synerising in a day.
2	0·6	Translucent jelly in 1½ min., which soon becomes opaque, and synerises in a day.
2	0·7	Opaque jelly in ½ min., synerising after 6 hrs.
2	0·8	,, ,, ,,
2	1·0	Opaque loose jelly in 1 min.
2	1·3	,, ,,
2	2·0	,, ,,
2	2·5	,, ,,
3	0·5	No jelly, clear solution.
3	0·7	Translucent jelly in 1 min.
3	1·0	Opaque jelly in 20 sec.
4	0·7	No jelly.
4	1·0	Opaque jelly in 10 sec.

TABLE XVIII.

Influence of Sulphate Ions.

M/2-Zirconium nitrate solution=2 c. c. Total volume=5 c. c.

Potassium-sulphate.	Sodium-acetate (3·54*N*).	Observation.
0 c. c.	0·4 c. c.	Clear solution, no jelly.
0·1	0·4	Translucent jelly in 5 minutes, no syneresis in 1 day.
0·2	0·4	Opaque jelly in ½ min.
0·3	0·4	Opaque jelly in 5 sec.
0	0·5	Translucent jelly in 4 min.
0·1	0·5	Opaque jelly in 1 min.
0	0·3	No jelly, clear solution.
0·5	0·3	Opaque jelly in ½ min.
0·7	0·3	White precipitate immediately but no jelly.

In this investigation of hydroxide jellies, we have tried to study the gelation properties in a comparative way by keeping the concentrations of the metallic halides or nitrates constant in all the cases. In view of the fact that the formation of jellies appears to be a function of the variable concentrations of no less than four different substances ; *e.g.*, metallic salts, sodium acetate, ammonia and ammonium sulphate, and also other numerous products of reaction, the whole system becomes very complex. It has been long known that when chromic chloride solution is boiled with sodium acetate and then made alkaline with caustic alkali, it sets to a jelly. Moreover, ferric, chromic and aluminium hydroxide sols are prepared by the addition of sodium acetate to their salts and dialysing the mixtures. The probable mechanism of the jelly formation with these hydroxides can easily be explained by assuming the formation of colloidal hydroxides by the interaction of metallic salts with sodium acetate.

The metallic hydroxides are stabilised by the absorption of metallic and hydrogen ions given out in the solution. In some cases the stability is so great, that any amount of the coagulating electrolyte is insufficient to neutralise the charge. However, by the addition of suitable amounts of ammonia, hydrogen ions are decreased and the system becomes more liable to coagulation.

In previous publications, we have shown in the cases of both hydrophobe and hydrophile colloids that under similar conditions, uncharged particles are more hydrated than the charged ones, and as the charge is gradually diminished, the sol becomes more and more viscous. Our results on the changes on viscosity during the process of gelation (*J. Indian Chem. Soc.*, 1929, 6, 391) of various inorganic jellies also support the view that as the charge is continuously neutralised, the system becomes more and more viscous. The function of ammonium sulphate in the above jellies is also similar. In the presence of a suitable concentration of hydrogen ions, ammonium sulphate brings about the gradual diminution of the positive charge of the particles, and as the charge diminishes, the system becomes more and more viscous, and finally a jelly is obtainted. Our results recorded in the previous tables show that there is always a fixed optimum range of the concentration of ammonium sulphate necessary for jelly formation. Any amount less than that will either give unstable loose jellies or precipitates. We have shown that after the neutralisation of the charge, the uncharged particles either tend to adsorb the solvent medium or to agglomerate with one another. In some cases in the presence of the coagulating electrolytes, both the tendencies of hydration and agglomeration go side by side and finally opaque jellies are obtained. By varying the concentrations of ammonium sulphate, we have shown that at higher concentrations of the electrolyte, the jellies produced are very loose, and in some cases, only precipitates have been obtained. This is due to the fact that the agglomeration tendency of the particles is preponderating over the hydration tendency in these cases.

As the stability of the colloidal metallic hydroxides produced by the action of sodium acetate and metallic salts depends upon the hydrogen ions adsorbed by them the time of gelation and the nature of the jelly are also affected by the hydrogen ion concentrations of the system. Thus the regulation of hydrogen ions is also a very important factor in the formation of these jellies. The results given in the two following tables show the comparative hydrogen ion concentrations of the metallic salt solutions and also of the same salt solutions when mixed with those amounts of sodium acetate which would give jellies on the addition of the proper amounts of ammonium sulphate and ammonia. Quinhydrone electrode and vernier potentiometer of Cambridge Instrument Co. were used to determine electromotive forces against normal potassium chloride—calomel electrode.

TABLE XIX.

8 C. c. of $M/2$-salt in 20 c.c.	*E.M.F.* in volts.	p_H.	c_H.
Ferric chloride	0·412	0·069	$8·53 \times 10^{-1}$
Chromic chloride	0·254	2·79	$1·62 \times 10^{-3}$
Aluminium nitrate	0·271	2·50	$3·16 \times 10^{-3}$
Zirconium nitrate	0·343	1·26	$5·49 \times 10^{-2}$
Stannic chloride	0·364	0·90	$1·26 \times 10^{-1}$

TABLE XX.

8 C.c. of $M/2$-solution of salts were taken. Total volume = 20 c.c.

Salts.	Sodium acetate added.	*E.M.F.* in volts.	p_H.	c_H.
Ferric chloride	3·6 c.c.	0·178	4·10	$7·95 \times 10^{-5}$
Chromic chloride	5·2	0·181	4·05	$8·91 \times 10^{-5}$
Aluminium nitrate	4·0	0·208	3·59	$2·57 \times 10^{-4}$
Zirconium nitrate	2·0	0·162	4·38	$4·16 \times 10^{-5}$
Stannic chloride	4·0	0·362	0·93	$1·17 \times 10^{-1}$

These results show that by the addition of sodium acetate to metallic salts, there is a considerable diminution in hydrogen ion concentration and a further diminution is observed when ammonia is added to the solution. The following table shows the hydrogen ion concentrations of the final systems which give rise to jellies.

TABLE XXI.

8 C.c. of $M/2$-salts taken. Total volume = 20 c.c.

Metallic hydroxide.	3·54*N*-Sodium acetate.	2*M*-Ammonium sulphate.	5·81*N*-Ammonia.	*E.M.F.* in volts.	p_H.	c_H.
Ferric	3·6 c.c.	2 c.c.	0·4 c.c.	0·155	4·50	$3·16 \times 10^{-5}$
Chromic	5·2	2	2·8	0·095	5·53	$2·95 \times 10^{-6}$
Aluminium	4·0	2·8	2·0	0·135	4·84	$1·44 \times 10^{-5}$
Zirconium	2·0	...	...	0·162	4·38	$4·16 \times 10^{-5}$
Stannic	4·0	2·0	...	0·351	1·12	$7·59 \times 10^{-2}$

The hydrogen ions of the initial metallic salt solutions of these five jelly-forming substances are in the following order:—

Ferric > stannic > zirconium > aluminium > chromic.

By the addition of sodium acetate, the order of the hydrogen ion concentrations becomes—

Stannic > aluminium > chromic > ferric > zirconium.

Finally, by the addition of all the necessary constituents of jelly formation, the order becomes—

Stannic > zirconium > ferric > aluminium > chromic. It shows that all the jellies cannot be obtained at the same hydrogen ion concentrations. The difference so obtained is to be explained on the basis of the intrinsic nature of the metals themselves. From our results on hydrogen ion concentrations, it appears that the metals which give jellies most readily are those which on the addition of sodium acetate, ammonia, etc., possess the system of the greatest hydrogen ion concentrations such as tin and zirconium. But the jellies which are obtained in a weaker hydrogen ion concentration medium, as iron, aluminium and chromium are the most stable and best in texture undergoing no marked syneresis.

In a previous paper (*loc. cit.*), we have classified the jellies on the basis of their transparency, and have stated that whenever the hydration tendency is the greatest, the jellies will be transparent, and the agglomeration tendency of the particles gives rise to opacity. Of the five hydroxide jellies investigated in this paper, aluminium hydroxide jellies, though opalescent are the most transparent. The zirconium hydroxide jellies are translucent when freshly formed but they become opaque in a few hours. Chromic hydroxide jellies are slightly translucent, though mostly opaque, while stannic and ferric hydroxide jellies are opaque. Thus the opacity of these jellies appears to be in the following order—

Stannic > ferric > chromic > zirconium > aluminium.

From this it appears that the hydration tendency of the particles is more marked in the case of aluminium and zirconium than in the case of chromium, iron, or tin.

The same method for the preparation of hydroxide jellies have been employed in the case of other metals like copper, cobalt, nickel, thorium, mercury and cadmium but the results so far obtained are negative. Weiser's preparation (*J. Phys. Chem.*, 1923, **27**, 685) of copper hydroxide jellies from copper acetate, ammonia, and

ammonium sulphate also appears to be similar to that of ours. It appears that with hydroxides of copper cobalt, nickel, cadmium and thorium, the tendency of the particles is more towards agglomeration than hydration, and the hydroxide colloids formed are very unstable and their particles do not develop marked hydration even when slowly coagulated.

Summary.

1. The jellies of iron, chromium, and aluminium hydroxides have been obtained by treating the metallic chlorides or nitrates with sodium acetate, ammonium sulphate and ammonia in suitable concentrations, the details of which have been investigated in a comparative way by varying the concentration of different jelly-forming constituents.

2. The jellies of zirconium hydroxide have been obtained by the addition of only sodium acetate to zirconium nitrate solution. The addition of sulphate ions favours the formation of this jelly; addition of ammonia is not necessary.

3. The jellies of stannic hydroxide have been obtained by the addition of sodium acetate and ammonium sulphate to stannic chloride solution. No addition of ammonia is necessary unless there is much free acid in the stannic chloride solution.

4. The mechanism of the formation of these hydroxide jellies has been explained on the assumption of the formation of colloidal hydroxides by the action of sodium acetate to the metallic salts, which are stabilised by the adsorption of metallic and hydrogen ions. The function of ammonia is to reduce the hydrogen ions to such an extent as to make the system liable to coagulation by ammonium sulphate. The ammonium sulphate gradually reduces the positive charge of the colloidal particles, and the system thereby becomes more viscous and hydrated, and finally the jellies are obtained.

5. All these jellies have been obtained in the acid medium. The comparative study of hydrogen ion concentrations of the jelly-forming systems shows that the jellies of different metals cannot be obtained at the same hydrogen ion concentrations. But the jellies most readily obtained are of those metals, as zirconium or tin, which on the addition of jelly-forming constituents give a medium of the greatest hydrogen ion concentrations. But these jellies are less

stable in comparison with those obtained in a medium of less hydrogen ion concentrations, as of the aluminium, chromium and iron.

6. The hydroxide jellies of nickel, cobalt, copper, cadmium, mercury and thorium could not be obtained as yet by the method used for the preparation of iron, chromium and other hydroxide jellies. It appears that in the case of these substances, the agglomeration tendency of the particles is more pronounced than the hydration tendency.

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Complex Ammoniacal Cobalt Molybdates.

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The preparation and properties of the complex cobalti-ammine molybdates have not been much studied evidently due to the nature of molybdate radicle, easily condensing into *iso*-poly complexes like di- and trimolybdates, which give rise to much complications. A cobalti-ammine molybdate of the empirical formula $Co_2O_3,7MoO_3$, $10NH_3,2H_2O$ has been described by Carnot (*Compt. rend.*, 1889 **109**, 112); no definite constitution has been ascribed to the compound. The only noteworthy investigation in the subject has been made by Paul and Sarkar (*Ann. Chim.*, 1926, **5**, 119). They have prepared and studied a large number of molybdates and polymolybdates of complex tetrammine cobaltic ion. Further, they have obtained evidences in a few cases where the molybdate or dimolybdate radicle forms a part of the cobaltic complex. In the case of pentammine series they succeeded in preparing one trimolybdate, one molybdate and one heptamolybdate of aquopentammine cobaltic complex. In the case of the tetrammine series they started either with the carbonatotetrammine cobaltic nitrate or the pure aquotetrammine cobaltic nitrate which by double decomposition with the normal sodium molybdate or sodium dimolybdate or ammonium molybdate gave the various compounds. In the case of the pentammine series also similar methods were followed. The present investigation was undertaken in order to make a more detailed study of the subject under conditions which would avoid complications due to the formation of *iso*-poly complexes by the molybdate radicle itself and thus would give rise to more well-defined compounds of normal molybdates free from the impurities of di- and trimolybdates.

The method adopted differed entirely from that of Paul and Sarkar. A mixture of the cobalt salt and normal sodium molybdate or molybdic acid in presence of calculated quantities of ammonium salt and ammonia was oxidised by the passage of a vigorous current of air through the solution, the crystals obtained were further purified by

repeated crystallisation from ammoniacal solution—thus preventing the formation of any polymolybdates. Barring two instances in which the normal molybdate radicle seemed to enter the complex, all the other compounds obtained were normal cobalti-ammine molybdates. The compounds obtained can be represented by the following constitutional formulae.

$\left[Cl{\cdot}Co{\cdot}(NH_3)_5 \right] MoO_4$ (I)

$\left[OH{\cdot}Co{\cdot}(NH_3)_5 \right] MoO_4 . 1 \text{ or } 2\tfrac{1}{2}\ H_2O$ (II)

$\left[H_2O{\cdot}Co{\cdot}(NH_3)_5 \right]_2 (MoO_4)_3$ (III)

$\left[MoO_4{\cdot}Co{\cdot}(NH_3)_5 \right]_2 MoO_4$ (IV)

$\left[\begin{matrix} H_2O \\ NO_2 \end{matrix} {\cdot}Co{\cdot}(NH_3)_4 \right] MoO_4$ (V)

$\left[\begin{matrix} MoO_4 \\ NO_2 \end{matrix} {\cdot}Co{\cdot}(NH_3)_4 \right]$ (VI)

$\left[SCN{\cdot}Co{\cdot}(NH_3)_5 \right] MoO_4$ (VII)

$\left[NO_3{\cdot}Co{\cdot}(NH_3)_5 \right] MoO_4$ (VIII)

Experimental.

Chloropentammine Cobaltic Molybdate (I).

Hydrated cobalt chloride (10 g.) was dissolved in water and to the resulting solution ammonium chloride (15 g.) was added, water being added in such quantity as to leave a portion of ammonium chloride undissolved. To this mixture, crystallised normal sodium molybdate (20 g.) made into a thin paste with water was stirred in (sodium molybdate was prepared by dissolving solid molybdic acid in caustic soda solution in stoichiometric proportions, filtering, evaporating the filtrate to a small bulk, draining away the mother-liquor and finally washing the crystals with alcohol to remove free alkali). To the mixture 70 c.c. of concentrated ammonia (*d* 0·9) were added. The mixture was kept at 15-20° and a rapid current of air was drawn in through the mixture till all solids dissolved. It was then filtered and

air was passed for four hours more. The mixture was then kept overnight in an ice-chest. Next day air was again passed for 5-6 hours more, by which time copious rose-red crystals separated. After allowing to settle for some time the mixture was filtered and the crystals were washed with 20% (by vol.) alcohol containing 2% ammonia and finally with absolute alcohol.

This substance could not be recrystallised. It was freely soluble in pure water when freshly prepared, but on attempting to evaporate the solution either on the water-bath, in air, or in vacuum, it decomposed. It was also freely soluble in ammoniacal water and from the solution a purple crystalline substance slowly separated which was insoluble in water. It was decomposed even by very dilute acids with the separation of free molybdic acid. It could not be salted out by a saturated solution of ammonium chloride as molybdate (MoO_4) group would be replaced by chlorine. With ammonium molybdate solution a gelatinous precipitate was obtained.

On the addition of alcohol to an ice-cold aqueous solution of the substance in the absence of ammonia a precipitate was obtained. But on an attempt to redissolve, it was found to be partly insoluble. On keeping for some weeks this precipitate was wholly converted into an insoluble variety identical with the insoluble product obtained from an ammoniacal solution. Treatment with aqueous alcohol at the room temperature led to the decomposition of the substance with separation of molybdic acid.

On analysis the crude compound gave the following results: Co, 17·6; MoO_4, 32·28; Cl, 18·5; NH_3, 25·9; H_2O, 5·8 per cent. corresponding to $Co_3(NH_3)_{15}Cl_5(MoO_4)_2,3H_2O$. The composition was however found to vary slightly in different preparations.

In solution it gave neutral reaction with litmus. Silver nitrate with dilute nitric acid in the cold gave with the solution of the freshly prepared substance at once a curdy white precipitate of silver chloride; the filtrate on heating gives further a very small quantity of silver chloride. Lead acetate acidified with a single drop of dilute acetic acid at once gave a precipitate of lead molybdate in the cold, the precipitate was difficult to filter; the filtrate on heating remained clear. The substance was found to belong to the pentammine series as it gave carmine-red crystals of chloropentammine chloride on evaporation with strong hydrochloric acid after the previous removal of molybdic acid by lead acetate and produced a red crystalline precipitate with ammonium oxalate. This crude substance on treatment

with dilute ammonia gave two products as described later on—the insoluble chloropentammine cobaltic molybdate (I) and the soluble hydroxopentammine cobaltic molybdate (II). From the behaviour of the substance it may be assumed that it is probably a mixture of

$$\left[H_2O{\cdot}Co{\cdot}(NH_3)_5 \right] Cl_3 \quad \text{and} \quad \left[H_2O{\cdot}Co{\cdot}(NH_3)_5 \right] \begin{matrix} Cl \\ MoO_4 \end{matrix}$$

(*i*) (*ii*)

in the approximate proportion of 1 : 2. The compound (*ii*) in solution, specially in presence of ammonia, gradually changes as follows:

$$2\left[H_2O{\cdot}Co{\cdot}(NH_3)_5 \right] \begin{matrix} Cl \\ MoO_4 \end{matrix} \rightleftharpoons \underset{\substack{\text{insoluble.} \\ \text{(I)}}}{\left[Cl{\cdot}Co{\cdot}(NH_3)_5 \right] MoO_4}$$

$$+ \underset{\text{soluble.}}{\left[OH{\cdot}Co{\cdot}(NH_3)_5 \right] MoO_4} + HCl + H_2O.$$

The presence of ammonia helps to shift the equilibrium completely to the right by the removal of hydrochloric acid. All attempts to prepare the pure aquopentammine chloromolybdate were unsuccessful on account of this partial dissociation. Attempt at separation in an acid medium on the other hand led to the separation of molybdic acid.

To a saturated aqueous solution of the rose-red mother-substance a few drops of ammonia were added, when a small quantity of purple crystals separated out. These were washed with water and dried in air. (Found: Co, 17·00; MoO_4, 47·32; Cl, 10·22; NH_3, 25·3. $[Cl{\cdot}Co{\cdot}(NH_3)_5]MoO_4$ requires Co, 17·38; MoO_4, 47·13; Cl, 10·46; NH_3, 25·03 per cent.).

This new substance had a deep purple colour and was insoluble in water. It gave very well-defined crystals. On shaking with silver nitrate in the cold the substance gradually went into solution yielding a white precipitate of silver molybdate soluble in dilute nitric acid, on warming the filtrate a curdy white precipitate of silver chloride was formed showing that the chlorine is inside and the molybdate radical is outside the complex zone. The substance gave carmine-red crystals of chloropentammine chloride on evaporation with concentrated hydrochloric acid. Hence the substance was found to be a chloropentammine molybdate.

Hydroxopentammine Cobaltic Molybdate (II).

On adding alcohol to the filtrate of the previous compound a precipitate was obtained; this was allowed to settle in a cold place and filtered. It was then dissolved in a small quantity of 4% ammonia and reprecipitated with alcohol. This was repeated once more. It was washed with 30% alcohol containing ammonia and finally with absolute alcohol. The red crystals obtained were dried over sulphuric acid. (Found: Co, 17·0; MoO_4, 48·49; NH_3, 25·1. $[OH{\cdot}Co{\cdot}(NH_3)_5]MoO_4,H_2O$ requires Co, 17·41; MoO_4, 47·2; NH_3, 25·07 per cent.).

The substance was found to be readily soluble in water and strongly alkaline to litmus. Lead acetate gave immediately a precipitate of lead molybdate in the cold—the filtrate yielded no further precipitate on acidification with a drop of acetic acid and heating. On removal of molybdenum with lead acetate, and of lead with excess of hydrochloric acid and evaporation of the resulting solution on the water-bath, carmine-red crystals of chloropentammine cabaltic chloride were obtained. These reactions proved it to be a hydroxopentammine cobaltic molybdate.

The same substance—but in a different state of hydration—was also obtained in the following way:

Hydrated cobalt nitrate (10 g.) and ammonium nitrate (22 g.) were dissolved together in the least quantity of water. Sodium molybdate (20 g.) was dissolved in strong ammonia (100 c.c.). The two solutions were mixed and filtered, cooled to 15° and into the solution a brisk current of air was passed till the black crystals of oxycobaltic compounds appeared. Then the mixture was heated to 40° and oxidation by air was continued till the black crystal disappeared giving rise to the formation of a red crystalline deposit. It was then left overnight in an ice-chest. Next day air was passed for two to three hours more; and the mixture was allowed to settle in a cool place and filtered. The red crystals obtained were washed with 30% alcohol containing 1% ammonia. For recrystallisation the mass was dissolved in 4% ammonia at 60°, the solution was cooled and a few drops of alcohol were added to induce crystallisation. It was then left in the ice-chest. Large silky crystalline plates were obtained; these were washed as before and dried in air to a constant weight. (Found: Co, 16·02; MoO_4, 43·45; NH_3, 23·19. $[OH{\cdot}Co{\cdot}(NH_3)_5]\ MoO_4$, $2\frac{1}{2}H_2O$ requires Co, 16·12; MoO_4, 43·71; NH_3, 23·22 per cent.).

On drying over sulphuric acid for three weeks it lost two molecules of water. This was found to be a better method of preparing this compound.

Aquopentammine Cobaltic Molybdate (III) *and Molybdatopentammine Cobaltic Molybdate* (IV).

Hydrated cobalt acetate (10 g.), made into a paste with 10 c.c. water and a little dilute acetic acid, was dissolved in 30 c.c. of concentrated ammonia (*d* 0·9). Ordinary crystallised ammonium molybdate (20 g.) was dissolved in 60 c.c. of concentrated ammonia. The two solutions were mixed and filtered. The filtrate was cooled to about 20° and a rapid current of air was drawn through it. Copious black crystals of oxycobalt-compounds separated after sometime, the temperature was then raised to 30-40° and ultimately to 50° and maintained at that point till all the black crystals disappeared and a large amount of a red crystalline substance separated. The mixture was then cooled to 10° and the oxidation by air was continued for sometime more. It was then allowed to settle in a cool place and filtered. The crystals were washed with dilute alcohol containing one per cent. ammonia. For recrystallisation the substance was dissolved in 10% ammonia at 70°, the solution was cooled and crystallisation was induced by adding alcohol. The crystals were filtered and washed with cold 1% ammonia and alcohol and dried in air. (Found: Co, 14·57; MoO_4, 59·76; NH_3, 21·22. $[H_2O{\cdot}Co{\cdot}(NH_3)_5]_2(MoO_4)_3$ requires Co, 14·68; MoO_4, 59·70; NH_3, 21·14 per cent.). It was fairly soluble in water and the solution was very faintly alkaline to litmus. This indicates that the substance is slightly hydrolysed by water as follows:

$$[H_2O{\cdot}Co{\cdot}(NH_3)_5]_2(MoO_4)_3 \rightleftharpoons 2[OH{\cdot}Co{\cdot}(NH_3)_5]MoO_4 + H_2MoO_4.$$

The hydroxo-compound evidently being more alkaline masks the week acid character of molybdic acid. Lead acetate or silver nitrate at once precipitated all the molybdenum in the cold. On heating to 100° it lost very little water but on gradually raising the temperature it was found to lose one molecule of water at 125-130° thus passing into a complex molybdatomolybdate. The dehydrated product was sparingly soluble in water, and when shaken with silver nitrate solution gave a precipitate of silver molybdate in the cold and the

filtrate on treating with a few drops of acetic acid and boiling gave a further precipitate of silver molybdate proving that a part of the molybdate radicle remained in the complex cation.

Paul and Sarkar (*loc. cit.*) described an insoluble aquopentammine cobaltic molybdate which in the light of the present work appears to be a hydrated molybdatopentammine molybdate. Lead acetate and nitrate solutions, as have been found, cannot decompose the insoluble molybdatopentammine molybdate and hence no molybdic acid could be detected in the filtrate after treating the compound with lead nitrate or acetate solution. This is possibly the reason why Paul and Sarkar supposed the insoluble compound to be an aquo-salt. It is more likely that Paul and Sarkar's compound contained no water at all. The insoluble compound is therefore proved to be a molybdatopentammine molybdate $[MoO_4 \cdot Co \cdot (NH_3)_5]_2Mo_4O$.

On prolonged digestion with water it passes into the aquopentammine molybdate and goes into solution.

Aquonitrotetrammine Cobaltic Molybdate (V) *and Nitrotetrammine Molybdatocobalt* (VI).

Hydrated cobalt acetate (10 g.) was triturated with 10 c.c. of water and a few drops of dilute acetic acid. This was then dissolved in 20 c.c. of concentrated ammonia (*d* 0·9). Sodium nitrite (3 g.) was dissolved in this solution, to which 7 g. of molybdic acid dissolved in conc. ammonia (60 c.c.) were added. The mixture was filtered. The filtrate was cooled to 15° and a rapid current of air was drawn through it till the black crystals of oxycobalt compounds appeared. Temperature was then raised to 25° and air was passed till all the black crystals disappeared. It was left overnight in an ice-chest, and air was passed again through the cold solution next day till copious red crystals separated. It was allowed to settle and then filtered. For recrystallisation the mass was dissolved in 6% ammonia and allowed to evaporate in air at the room temperature. The crystals seprated were washed with 1% cold ammonia. (Found: Co, 16·63; MoO_4, 44·81; NH_3, 19·72; N, 19·95. $[NO_2(NH_3)_4 \cdot Co \cdot H_2O]\ MoO_4$ requires Co, 16·81, MoO_4, 45·58 ; NH_3, 19·37; N, 19·95 per cent.).

The light red-coloured substance was found to be sparingly soluble in water. The whole of the molybdate radicle was precipitated in the cold by neutral lead nitrate or silver nitrate solution, proving

the molybdate radicle to be outside the complex zone. On heating to about 96° in a steam-oven it lost one molecule of water and became more sparingly soluble. The colour of the crystals also became slightly dull. Evidently the dehydrated product was a nitrotetrammine molybdatocobalt of the formula,

$$\left[MoO_4 \cdot Co \begin{matrix} NO_2 \\ (NH_3)_4 \end{matrix} \right].$$

But on digesting it with either neutral lead nitrate or silver nitrate solution the whole of the molybdate was removed. It, therefore, indicates that the substance is easily hydrolysed in water into original aquonitrotetrammine cobaltic molybdate as follows:—

$$\left[MoO_4 \cdot Co \begin{matrix} NO_2 \\ (NH_3)_4 \end{matrix} \right] + H_2O \longrightarrow \left[H_2O \cdot Co \begin{matrix} NO_2 \\ (NH_3)_4 \end{matrix} \right] MoO_4.$$

Thiocyanatopentammine Cobaltic Molybdate (VII).

Cobalt acetate crystals (10 g.) were dissolved in 10 c.c. of water and 20 c.c. of concentrated ammonia (*d* 0·90); to this was added a solution of ammonium thiocyanate (4 g.) in 10 c.c. of water. A solution of ammonium molybdate (8 g.) was made in strong ammonia (70 c.c.) and the two solutions were mixed and filtered. The filtrate was cooled and a rapid current of air was drawn through it. Black crystals of oxycobalt compounds separated as before when the temperature was raised to 30-40°. These then gradually disappeared. The solution was then left overnight in a cool place. Next day air was passed again through the solution at 10° when large quantities of red crystals separated. The mixture was then filtered after allowing it to settle in a cool place. The substance was purified by recrystallisation from 6% ammonia at 60°. The crystals obtained were washed with cold 1% ammonia and dried in air. (Found: Co, 15·97; MoO_4, 43·86; NH_3, 22·79; SCN, 15·57; $[SCN \cdot Co \cdot (NH_3)_5] MoO_5, \frac{1}{2}H_2O$ requires Co, 15·91 ; MoO_4, 43·12. NH_3, 22·91; SCN, 15·63 per cent.). Another sample dried in air to a constant weight gave Co, 16·14. $[SCN \cdot Co \cdot (NH_3)_5]MoO_4$ requires Co, 16·30 per cent.; so that the latter is anhydrous.

The dark red crystals were found to be sparingly soluble in water and neutral to litmus. On digesting the substance with silver nitrate

solution in the cold the whole of the molybdate and the thiocyanate were removed indicating that the substance readily hydrolysed in water into an aquopentammine cobaltic thiocyanatomolybdate,

$$\left[SCN{\cdot}Co{\cdot}(NH_3)_5\right] MoO_4 + H_2O \longrightarrow \left[\, H_2O{\cdot}Co{\cdot}\,(NH_3)_5 \,\right] \begin{matrix} SCN \\ MoO_4 \end{matrix}.$$

Nitratopentammine Cobaltic Molybdate (VIII).

Hydrated cobalt nitrate (10 g.) was dissolved in water (20 c.c.) and ammonium nitrate (4 g.) was added to it. Ammonium molybdate (7 g.) dissolved in 60 c.c. of ammonia (*d* 0·9) was then added and the mixture was filtered rapidly. The filtrate was cooled to 20° and a rapid current of air was drawn through it till black crystals of oxycobaltcompounds separated out. Temperature was then raised to 40° and the passage of air-current was continued till all the black particles disappeared. It was then filtered and left overnight. Next day air was again passed through the cold solution till copious red crystals separated. The mixture was then filtered after allowing to settle in a cool place. For recrystallisation it was dissolved in 6% ammonia at 60° and allowed to evaporate spontaneously in air. The crystals separated were washed first with cold 20% alcohol containing ammonia and finally with absolute alcohol. They were then dried in the air. (Found: Co, 16·01; MoO_4, 43·99; NH_3, 23·01; N, 22·91. $[NO_3{\cdot}\,Co{\cdot}(NH_3)_5]MoO_4$ requires Co, 16·12; MoO_4, 43·71; NH_3, 23·22; N, 22·95 per cent.).

The substance was found to be soluble in water and neutral to litmus. Lead acetate immediately precipitated the whole of the molybdenum in the cold proving it to be a nitratopentammine cobaltic molybdate.

Method of Analysis.

In the above compounds cobalt was always estimated volumetrically. The compounds were decomposed by digesting on the water-bath with excess of pure caustic soda, and the cobaltic oxide, after being thoroughly washed free from alkali was treated with potassium iodide solution and acidified with dilute sulphuric acid, and the liberated iodine was titrated against standard thiosulphate. The filtrate was treated with excess of liquor ammonia and then saturated with sulphuretted hydrogen. On acidification and being heated on the

water-bath the molybdenum was precipitated as sulphide; it was filtered, washed converted into trioxide by ignition and weighed as such. Chlorine was estimated as silver chloride in the filtrate from molybdenum, after removing the sulphuretted hydrogen by evaporation and treatment with ammoniacal hydrogen peroxide. Ammonia was always estimated by distillation with caustic soda. Total nitrogen was estimated by combustion. To estimate the thiocyanate group the compound was broken up with pure caustic soda, and the filtrate was treated with hydrogen peroxide to oxidise the thiocyanate; molybdenum was then precipitated, after neutralising the solution carefully with nitric acid, by excess of silver nitrate; and the excess of silver was removed by hydrochloric acid, and in the filtrate sulphur was precipitated by barium chloride after the removal of nitric acid by evaporation with hydrochloric acid.

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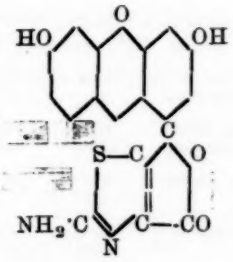
Dyes derived from 2-Aminothiazole-4:5-dicarboxylic Acid.

By Satish Chandra De.

The object of the present communication was to prepare fluoresceines, eosines and rhodamines from 2-aminothiazole-4:5-dicarboxylic acid similar to those obtained from phthalic anhydride, quinolinic acid, succinic acid, iminazoledicarboxylic acid, itaconic and citraconic acids, with a view to compare their colour and fluorescence.

2-Aminothiazoledicarboxylic acid condenses with aromatic amino- and hydroxy-compounds directly and it has been found that the addition of condensing agents such as sulphuric acid and zinc chloride does not give better yield. The constitution of these compounds can be represented as follows, taking resorcinolaminothiazomalein as a typical representative.



Resorcinolaminothiazomalein.

The following aromatic amino- and hydroxy-compounds have been condensed with the aminothiazoledicarboxylic acid and the corresponding thiazomaleins obtained:—resorcinol, catechol, phloroglucinol, orcinol, amidophenol and *m*-dimethyl-*m*-amidophenol. The condensation product with resorcinol has been brominated and the corresponding tetrabromo-compound obtained.

Two compounds are probably formed by the condensation of 2-aminothiazoledicarboxylic acid with resorcinol, one of which is brown and the other green. The former is the true resorcinolamino-

thiazomalein which dissolves in alkali with a green fluorescence whilst the latter, which is formed only in traces, does not exhibit any fluorescence in alkaline solution. It might be a substance resembling 1:3-dihydroxyanthraquinone in constitution (*cf.* Ghosh, *J. Chem. Soc.*, 1919, **115**, 1102).

As in these compounds the double bonds are in juxtaposition, it is very probable that in accordance with the theory of molecular strain, the intensity of their colour should be very similar to those of the citraconeins (Dhar and Dutt, *J. Indian Chem. Soc.*, 1927, **4**, 253), and in fact, in general properties, colour and fluorescence it appears that dyes derived from 2-aminothiazoledicarboxylic acid are similar to those of the corresponding substances obtained from citraconic acid.

Experimental.

The condensations of 2-aminothiazole-4:5-dicarboxylic acid with the aromatic hydroxy-and amino-compounds have been effected by direct heating of the components at temperatures varying between 170° and 200°. The results of experimental observations are summarised below:—

Name.	Appearance.	M.p.	Colour in alkali.	Colour of fluorescence.	Analysis: calc % in brackets.
Resorcinol ...	Reddish-brown rectangles.	246°	Orange-red	Green	N, 7·91 (8·12)
Catechol ...	Black-brown rectangles.	Above 298°	Pinkish-red	...	N, 7·53 (7·72)
Phloroglucinol ...	Grey needles	Above 298°	Red	...	N, 7·25 (7·46)
Orcinol ...	Grey powder	Above 300°	Orange-red	Green	—
m-Amidophenol	Grey rectangles.	Above 300°	Red	Faint pink	N, 11·90 (12·03)
Dimethyl-*m*-amido phenol	Brick-red	Above 300°	Magenta	Faint pink	N, 13·73 (13·82)
Tetrabromo-resorcinol	Brick-red	210°	Pink	Yellow-green	N, 4·19 (4·41)

My thanks are due to Prof. J. C. Ghosh and Dr. P. C. Guha for their kind interest and encouragement during the progress of this work.

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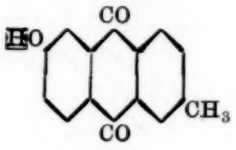
Studies in the Anthraquinone Series. Synthesis of Anthraquinones related to Morindone and Emodin.

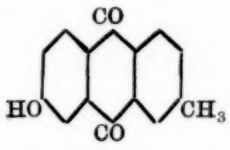
By Prafulla Chandra Mitter and Asoke Kumar Sarkar.

In a recent communication (*J. Indian Chem. Soc.*, 1928, **5**, 769) it has been shown by Mitter and Biswas that anthraquinone derivatives occurring in plants could be classified under four types, *viz.*, the chayroot, madder, morindone and emodin types. In the case of the chayroot and the madder types it has been further shown that the anthraquinones actually form links in oxidation and reduction chains of which the β-monosubstituted or the $\beta\beta'$-disubstituted products are the first members.

It appeared to us to be of interest to enquire whether the heteronuclear anthraquinones belonging to the morindone and emodin types could also be constituted into similar oxidation and reduction chains and we thought of studying in this connection 2-hydroxy-6-methyl- and 3-hydroxy-6-methylanthraquinones (I and II) and also 1-hydroxy-6-methylanthraquinone (III), which might be regarded as possible starting points for such chains.



(I)



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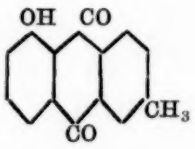
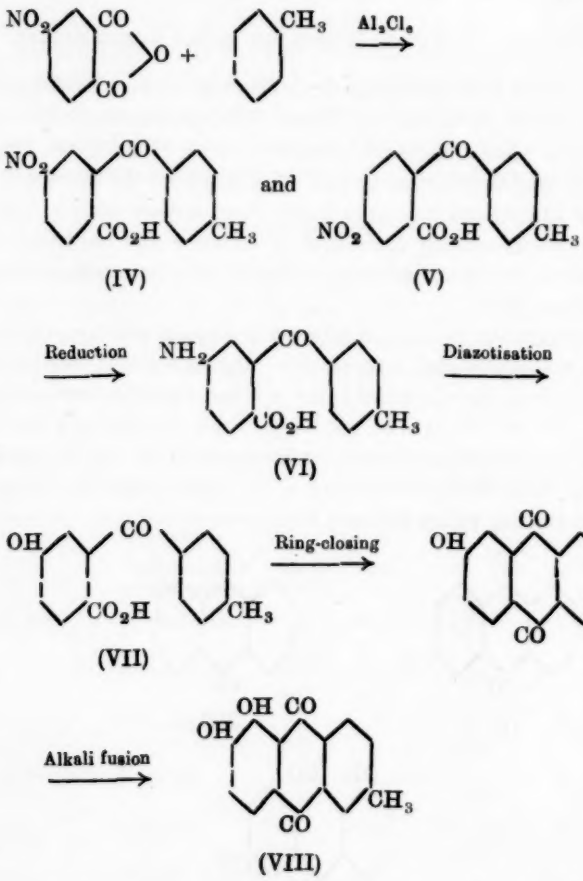


(III)

The first of these groupings is present in morindone, the second in emodin while the third contains a grouping which is common to both these types.

The methods of oxidation which we proposed to employ for realising the links in the oxidation series were, besides direct oxidation, indirect methods of oxidation, namely, over the nitro-derivatives.

The syntheses of 2-hydroxy-6-methyl- and 3-hydroxy 6-methylanthraquinones were attempted according to the following scheme.—



Similarly from (V) by an identical series of reactions, we hoped to get 3-hydroxy-6-methylanthraquinone (II).

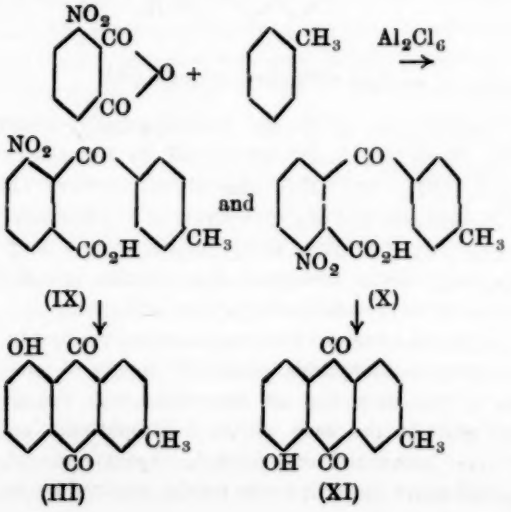
It was found however that the condensation of 4-nitrophthalic anhydride with toluene leads to the formation of only one nitrotoluoylbenzoic acid to which must be ascribed the constitution (IV) as

the anthraquinone (I) obtained from it gave on alkali fusion a product (VIII) which is identical with the anthraquinone prepared by Mitter and Biswas (*loc. cit.*) by condensing hemipinic anhydride with toluene and to which the formula (VIII) has been ascribed by the authors.

The mother-liquor after the crystallisation of the above nitrotoluoylbenzoic acid contained a small quantity of a substance having a lower melting point (not sharp) which was not further investigated.

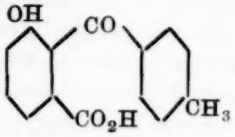
Quite in keeping with our expectations, a dinitro-compound was formed by nitrating the anthraquinone (I) after methylation. This however after replacement of the nitro-groups by methoxyl groups by the method of Kaufler (*Ber.*, 1904, **37**, 65) yielded, on de-methylation, a compound which though resembling morindone in having an orange colour, being crystallisable from toluene and in giving a violet coloration with alkalis resembling that of alizarin, melted between 240° and 245° whereas pure morindone melts at 271-72°. The quantity of the substance at our disposal being small, it could not be further investigated.

As regards 1-hydroxy-6-methylanthraquinone, we attempted its synthesis by condensing 3-nitrophthalic anhydride with toluene which was expected to give us two nitrotoluoylbenzoic acids leading ultimately to the synthesis of 1-hydroxy-6-methyl and 1-hydroxy-7-methylanthraquinone.

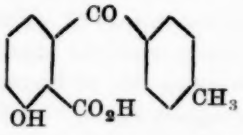


The condensation in this case gave rise, however, to only one product.

An indirect evidence of its constitution was furnished by the fact that the hydroxytoluoylbenzoic acid obtained from it did not give any colour reaction with alcoholic ferric chloride thus pointing to its possessing the structure (XII),



(XII)

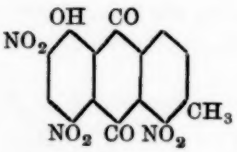


(XIII)

rather than (XIII) in which the hydroxyl group would lie adjacent to the carboxyl group.

It follows therefore that the anthraquinone derived from it must have the formula (III). Attempts at conversion of (III) into (VIII) by alkali fusion failed.

The nitration of (III) gave rise to a trinitro-derivative which is probably



judging from its analogy with chrysophanic acid.

The condensation of 3- and 4-nitrophthalic anhydrides with toluene has been previously attempted by Lawrence (*J. Amer. Chem. Soc.*, 1921, **43**, 2577) who claims to have obtained two products in each case and describes them as " brownish amorphous powders which do not have sharp melting points and decompose on melting and while somewhat more soluble in cold than in hot alcohols they do not crystallise from these solvents."

As already mentioned, the condensation product in the case of the 4-nitrophthalic anhydride consisted *mainly* of one compound (and this is the only fact in agreement with the statements of Lawrence) while in the case of the 3-nitrophthalic anhydride exclusively one compound was formed. Again none of the statements quoted above conform to the results obtained by us.

The nitrotoluoylbenzoic acid (IV) crystallised from dilute acetic acid in small white crystals melting sharply at 171°. The nitrotoluoylbenzoic acid (IX) crystallised from dilute alcohol in glistening pale yellow scales melting sharply at 219°. We have looked for its isomer in the mother-liquors with negative results. Moreover the melting points of our compounds do not agree with those given by Lawrence for his toluoylbenzoic acids, which were evidently impure tarry products.

A very singular fact has come to light in connection with the 4-nitrophthalic anhydride condensation. As usual, the condensation was attempted in presence of anhydrous aluminium chloride. Every time however the experiment failed, the whole reaction mixture being converted into a tarry mass. The effect of temperature was studied and it was found that even with ice-cooling the result did not improve. Regulation of the quantity of aluminium chloride similarly proved to be ineffective. It then somehow occurred to us that our aluminium chloride was in some inexplicable way acting prejudicially in the reaction and as we had been employing fresh specimens all along we thought of moderating the reaction by the use of old specimens tempered by partial absorption of moisture from the atmosphere. To our surprise, the reaction this time proceeded smoothly and we could isolate the product in quite pure condition, the formation of tar being almost nil. In all our subsequent operations we used this partially hydrated aluminium chloride with uniform success. That the presence of moisture was the determining factor in the success of the condensation has been definitely proved by direct addition of a few drops of water to the reaction mixture in cases where formation of tar seemed inevitable (by noting the change from the normal green to the brown-red coloration of tar) owing evidently to the fact that the aluminium chloride used was not sufficiently hydrated. In all such cases the usual green colour was restored and the condensation proceeded smoothly.

As regards the 3-nitrophthalic anhydride condensation, Lawrence used the temperature of the boiling water-bath. By conducting the experiment at that temperature we have found that the formation of tar is very large so that the product presents the appearance of a 'brownish amorphous substance' the purification of which could not obviously be effected by the author. After several trial experiments the optimum temperature was found to lie between 40° and 45° at which tar formation was considerably diminished and the

product consisted of a brown plastic mass, much easier of purification.

Then, the method of purification employed by Lawrence is evidently unsatisfactory. Though he admits that he could not crystallise the substances and effected a " somewhat unsatisfactory separation " of the supposed isomers in each case, by methyl alcohol he did not apparently adopt any special means of purification for his toluoylbenzoic acids. We have on the other hand found it essential to go through a course of tedious purifying operations (specially in the case of the product from 3-nitrophthalic anhydride) before we could obtain the substances in a crystallisable condition. Of these, extraction by boiling with excess of calcium carbonate constitutes an important step, by far the greatest amount of purification being attained here.

Experimental.

Preparation of 3- *and* 4-*Nitrophthalic Acids.*—These were prepared by the method of Lawrence (*J. Amer. Chem. Soc.*, 1920, **42**, 1871). Phthalic acid was nitrated with fuming nitric acid when a mixture of 3- and 4-nitrophthalic acids was obtained. These were separated by the method of Miller (*Ber.*, 1878, **11**, 393). The 4-nitrophthalic acid thus obtained melted at 159-61° and was almost pure.

Prepartion of 4-*Nitrophthalic Anhydride.*—This was prepared by the method of Bogert and Boroschek (*J. Amer. Chem. Soc.*, 1901, **23**, 743) with some modification. 4-Nitrophthalic acid was heated in a stout distilling flask, to 190-95° in vacuum, until frothing ceased and a clear melt was obtained. This was poured out and refluxed with acetyl chloride while still in a semi-solid condition. The solution deposited crystals of 4-nitrophthalic anhydride on cooling, m.p. 112-14°. (The pure substance melts at 114°).

3-*Nitro*-2-p-*toluoylbenzoic Acid.*—3-Nitrophthalic anhydride (7·5 g.) prepared according to the method of Eder and Widmer (*Helv. Chim. Acta*, 1922 **5**, 10) was suspended in toluene (100 c.c.) and to this aluminium chloride (15 g.) was added in small portions at a time and then the flask was heated on a water-bath at 40-50° for 5 hours. The contents of the flask were then acidified with 10% hydrochloric acid (135 c.c.) and the excess of toluene distilled off by passing in steam. The crude toluoylbenzoic acid was extracted by

hot sodium carbonate solution (100 c.c. of 10%). On acidifying with hydrochloric acid (10 %) a plastic mass was obtained which was dissolved in hot acetic acid, boiled with the addition of a little animal charcoal and filtered. On dilution with water a greenish precipitate was obtained contaminated with tarry matter which was boiled with calcium carbonate and filtered. On acidifying the filtrate a light yellow precipitate of the toluoylbenzoic acid (IX) was formed. Crystallised from dilute alcohol 3·5 g. of the acid, m.p. 218-19°, were obtained as pale yellow crystalline plates. (Found: N, 5·06. $C_{15}H_{11}O_5N$ requires N, 4·91 per cent.).

3-*Amino*-2-p-*toluoylbenzoic Acid*.—Ferrous sulphate (32 g.) was dissolved in water (210 c.c.) in a wide mouthed flask, boiled and concentrated ammonia (50 c.c.) then added. To the precipitated ferrous hydroxide a warm solution of the nitrotoluoylbenzoic acid (4·5 g.) in concentrated ammonia (45 c.c.) was added, heated for 15 minutes and filtered. The filtrate was boiled to drive off ammonia. To the boiling solution a hot solution of alum (4·5 g.) in water (45 c.c.) was gradually added and the whole filtered hot, when yellow prismatic crystals of the aminotoluoylbenzoic acid (2 g.) were obtained. Recrystallised from water it melted at 165°. (Found: N, 5·81. $C_{15}H_{13}O_3N$ requires N, 5·49 per cent.).

3-*Hydroxy*-2-p-*toluoylbenzoic Acid*.—The amino-acid (2 g.) was dissolved in dilute ammonia by warming and dilute hydrochloric acid added until the precipitate first formed dissolved away. The bright yellow solution of the hydrochloride was cooled to 0° and the calculated quantity of a solution of sodium nitrite (0·6 g.) in water (7 c.c.) gradually added while stirring the mixture by a mechanical stirrer. The precipitated diazonium salt was decomposed by boiling for 15—20 minutes, a little animal charcoal added and the whole filtered hot, when silky yellow needles of the hydroxy acid (1·5 g.) were obtained. Recrystallised from ethyl acetate and petroleum ether it melted at 225-26°. It does not give any coloration with alcoholic ferric chloride. (Found: C, 70·43; H, 4·55. $C_{15}H_{12}O_4$ required C, 70·31; H, 4·69 per cent.).

1-*Hydroxy*-6-*methylanthraquinone*.—To the hydroxytoluoylbenzoic acid (2 g.) was added boric anhydride (2 g.) and sulphuric acid (4 g., *d* 1·84). To the mixture was then added fuming sulphuric acid (20 g., 20 % SO_3) and heated on the water-bath for 3 hours. This was then poured into ice when an orange mass was obtained, which was extracted first with boiling water to remove boric acid

and then with a cold 5% solution of sodium carbonate. The crude anthraquinone on crystallisation from glacial acetic acid gave bright yellow needles melting at 147°. (Found: C, 75·4 ; H, 4·2. $C_{15}H_{10}O_3$ requires C, 75·63; H, 4·2 per cent.).

The *acetyl* derivative crystallised from alcohol, m.p. 172°. The anthraquinone obtained on de-acetylation melted at 147°. (Found: C, 72·71; H, 4·33. $C_{17}H_{12}O_4$ requires C, 72·86; H, 4·29 per cent.).

2:4:5(?)—*Trinitro-1-hydroxy-6-methylanthraquinone.*—1-Hydroxy-6-methylanthraquinone (0·5 g.) was intimately mixed with potassium nitrate (0·5 g.) and concentrated sulphuric acid (3 g.) added. The mixture was then heated on a water-bath for 5 hours. The nitro-compound after washing with hot water crystallised from glacial acetic acid, in tiny, golden yellow crystals, m.p. 285-86°. (Found: N, 11·39. $C_{15}H_7O_9N_3$ requires N, 11·26 per cent.).

4-*Nitro*-2-p-*toluoylbenzoic Acid.*—4-Nitrophthalic anhydride (7·5 g.) was suspended in toluene (100 c.c.) and to this partially hydrated aluminium chloride (18 g.) was added in small portions during the course of an hour, the flask being shaken continuously all the time. The mixture turned deep green and was then heated on a water-bath at 50-60° for 5 hours. The contents of the flask were then acidified with hydrochloric acid (135 c.c. of 10%) and the excess of toluene distilled off with steam. The crude acid was extracted by hot sodium carbonate solution (100 c.c. of 10%). On acidifying a semi-solid mass (7 g.) was obtained which hardened on keeping. Crystallised from acetic acid, tiny white prisms, m.p. 171°, were obtained. (Found: N, 5·08. $C_{15}H_{11}O_5N$ requires N, 4·91 per cent.).

4-*Amino*-2-p-*toluoylbenzoic Acid.*—The reduction of the 4-nitro-acid (4·5 g.) was carried out exactly in the manner employed with the corresponding 3-nitro-acid. Crystallised from water it formed light yellow plates, m.p. 175° (yield, 1·3 g.). (Found: N, 5·67. $C_{15}H_{13}O_3N$ requires N, 5·49 per cent.).

4-*Hydroxy*-2-p-*toluoylbenzoic Acid.*—The amino-acid (2 g.) was dissolved in dilute ammonia by warming and dilute hydrochloric acid added until the precipitate first formed dissolved. The solution was cooled to 0° and sodium nitrite (0·6 g.) in water (7 c.c.) gradually added while stirring the mixture mechanically. The solution was then boiled for 15-20 minutes, a little animal charcoal added and filtered hot. An oily precipitate was formed which changed to tiny white crystalline plates on cooling (yield, 1·5 g.). Crystallised from

water it melted at 182-83°. (Found: C, 70·51; H, 4·64. $C_{15}H_{12}O_4$ requires C, 70·31; H, 4·69 per cent.).

2-*Hydroxy*-6-*methylanthraquinone*.—The hydroxytoluoylbenzoic acid was mixed with boric anhydride and sulphuric acid as in the preparation of 1-hydroxy-6-methylanthraquinone and heated in glycerol-bath at 90-95° for 3 hours. This was then poured into ice when a green mass was obtained which was extracted with hot water. The crude anthraquinone on crystallisation from alcohol gave golden yellow plates (1·5 g.) melting at 278°. (Found: C, 75·49; H, 4·33. $C_{15}H_{10}O_3$ requires C, 75·63; H, 4·2 per cent.).

Alkali Fusion of 2-*Hydroxy*-6-*methylanthraquinone*.—2-Hydroxy-6-methylanthraquinone (1 g.) was heated in a nickel crucible with potassium hydroxide solution (10 c.c. of 50%) at 185-95° for $1\frac{1}{2}$ hours with addition of sodium arsenate (2 g.) from time to time. The violet coloured melt was extracted with hot water, acidified and filtered. The precipitate of the dihydroxymethylanthraquinone was extracted by heating with baryta water and the barium-lake decomposed by acid. The process was repeated thrice. The anthraquinone was then dissolved in acetic acid, boiled with the addition of animal charcoal, filtered and the filtrate precipitated with water. The operation was repeated. The precipitate thus obtained was sufficiently pure for crystallisation from glacial acetic acid, when yellow crystals melting at 218-19° were obtained. The m.p. remained unchanged on mixing with 1:2-dihydroxy-6-methylanthraquinone.

2-*Acetoxy*-6-*methylanthraquinone*.—This was prepared in the usual way. Light yellow plates, m.p. 145-47° were obtained on crystallisation from alcohol. (Found: C, 72·51; H, 4·48. $C_{17}H_{12}O_4$ requires C, 72·86; H, 4·29 per cent.).

2-*Methoxy*-6-*methylanthraquinone*.—The hydroxymethylanthraquinone (2 g.) was dissolved in sodium hydroxide solution (6 c.c. of 10%) by warming and dimethyl sulphate (2 c.c.) added, the mixture being shaken well after the addition. Excess of sodium hydroxide solution was then added and the flask heated on the water-bath for an hour. The contents were afterwards boiled with water and filtered. The crude methoxyanthraquinone on crystallisation from alcohol gave yellow needles melting at 177° (yield 1·5 g.). (Found: C, 75·88; H, 4·81. $C_{16}H_{12}O_3$ requires C, 76·19; H, 4·76 per cent.).

Dinitro-2-methoxy-6-methylanthraquinone.—2-Methoxy-6-methylanthraquinone (0·5 g.) was mixed with powdered potassium nitrate (0·5 g.) and concentrated sulphuric acid (3 g.) added. The mixture was heated on a water-bath for 5 hours. The nitro-compound was boiled with water, filtered and crystallised from acetic acid, m.p. 260-62°. (Found: N, 7·88. $C_{16}H_{10}N_2O_7$ requires N, 8·19 per cent.).

Trimethoxy-6-methylanthraquinone.—The above nitro-compound (0·5 g.) was suspended in absolute methyl alcohol (15 c.c.) and a solution (20 c.c.) of potassium methoxide (prepared by adding 1 g. of potassium to 20 c.c. of absolute methyl alcohol) added. The mixture was heated on the water-bath with reflux condenser for 6 hours and then poured into water (120 c.c.), filtered after boiling and the methoxyanthraquinone obtained was thoroughly dried. The crude product melted at 230-35° and was treated as described below.

Trihydroxy-6-methylanthraquinone.—The substance was intimately mixed with finely powdered aluminium chloride (1·5 g.) and heated to 230° in the course of one hour and then kept at this temperature for half an hour more. When cooled the mixture was transferred to a beaker, using ice-cold water and then boiled with a few c.c. of concentrated hydrochloric acid. The residue was collected, dissolved in potassium hydroxide solution (1%), filtered and the filtrate acidified, when thick yellow flakes appeared on boiling. Crystallised from toluene, the orange coloured product melted between 240° and 245°. It gave a beautiful violet coloration in alkaline solution.

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Nitration. Part IV. Nitration by Means of a Mixture of Nitrosulphonic and Fuming Nitric Acids.

By P. S. Varma and Shyamkishore Sharma.

In a previous communication (Varma and Kulkarni, *J. Amer. Chem. Soc.*, 1925, **47**, 143) it has been shown that a mixture of nitrosulphonic and fuming nitric acids can be used as a nitrating agent and a number of nitro-derivatives could thus be obtained. The yield of the nitro-compounds so obtained was found to be quantitative in several cases and the products were, as a rule, free from by-products. Attempts have been made in this paper to study further the action of this nitrating agent on some more complex organic compounds. Two difficulties have been found in the experiments carried on in this connection. In some cases the reaction is so vigorous that special care has to be taken for preventing the charring of reacting mixture. This has been done either by adding an inert solvent such as chloroform or carbon tetrachloride to the reacting substance or by a very careful addition of the nitrating agent. To prevent charring at the end of the operation due to the action of the reacting mixture with water, the reaction products had to be handled very carefully in some cases.

From *p*-nitrophenol, sulphanilic acid, *o*-, *m*- and *p*-aminobenzoic acids, *p*-dibromobenzene, benzoin, hydroquinone, cinnamic acid, α-nitronaphthalene, *p*-chlorophenol and *p*-iodotoluene, definite products have been obtained, though not necessarily the nitro-derivatives.

Experimental.

The nitrosulphonic acid mixture is prepared by passing a stream of sulphur dioxide into cold fuming nitric acid (*d* 1·502) until a mixture containing about 50 per cent. of nitrosulphonic acid is obtained. Most of the experiments described have been carried on at the room temperature (25-30°). The substance to be experimented upon is placed in a flask and dissolved in an inert solvent if

necessary and the nitrating mixture added drop by drop and shaken vigorously after each addition. If the reaction is too vigorous, the flask is cooled under tap water. When the whole of the nitrating mixture has been added, the flask is shaken frequently for another 15 minutes and warmed for a few minutes on a water-bath. The product is then diluted with water and the solid, if separated, is removed by filtration, washed and crystallised from some suitable solvent and identified. The results obtained are summarised in the table given below.

TABLE I.

Substance.	Amount of nitrating mixture added.	Product.
p-Nitrophenol (5 g.)	20 g.	2 :4-Dinitrophenol (1·5 g.)
Sulphanilic acid (10 g.)	,,	*p*-Nitrophenol (2 g.) 2 :4-Dinitrophenol (2·5 g.) 2 : 4 : 6-Trinitrophenol (0·5 g.)
o-Aminobenzoic acid (10 g.)	,,	Salicylic acid (5 g.)
m-Aminobenzoic acid (5 g.)	5 g.	3-Hydroxy-4-nitrobenzoic acid (1·5 g.)
p-Aminobenzoic acid (5 g.)	10 g.	4-Hydroxy-3-nitrobenzoic acid (2 g)
p-Dibromobenzene (2 g.)	5 g.	2-Nitro-1 : 4-dibromobenzene (1·5 g.)
p-Chlorophenol (2 g.)	3 g.	4-Chloro-2-nitrophenol (2·1 g.)
Cinnamic acid (4 g.)	10 g.	*o*-Nitrocinnamic acid (1·1 g.); *p*-nitrocinnamic acid (1·5 g.)
α-Nitronaphthalene (8 g.)	25 g.	1 : 3-Dinitronaphthalene (2·1 g.) 1 : 5-Dinitronaphthalene (1·5 g.)
p-Iodotoluene (5 g.)	10 g.	*p*-Nitrotoluene (2·1 g.)
Benzoin (5 g.)	5 g.	Benzil (3·0 g.)
Hydroquinone (5 g.)	5 g.	Quinhydrone (1 g.); benzoquinone (1·1 g.)

With *p*-nitrophenol, the reaction is so vigorous that the reacting mixture required to be cooled under water, but it is comparatively smooth and on pouring the reacting mixture into water, 2 :4-dinitrophenol crystallises out.

With sulphanilic acid the reaction is still more vigorous and the whole mass is charred if great care is not taken in adding the nitrating mixture very carefully. The product, after the addition of the nitrating mixture, is diluted with water very carefully and heated on a water-bath for about half an hour. There is a considerable frothing at this stage and the vessel is to be removed from the

water-bath from time to time so as to prevent the charring of the product. The solid separated is then fractionally crystallised from acetic acid and the crystals identified. Some more solid is obtained from the residual solution.

With *o*-aminobenzoic acid the reaction is so vigorous that each drop of the nitrating mixture produces a slight explosion and charring. By adding a few c.c. of chloroform, however, the reaction is moderated so that the formation of a tarry product is to a considerable extent prevented. From the resulting mass salicylic acid is extracted by boiling water and crystallised.

With *m*-amino- and *p*-amino-benzoic acids also the reaction is very vigorous. The substances are therefore dissolved first in chloroform (10 c.c.) and the sulphuric acid from the end products removed by the addition of barium chloride before they are concentrated and crystals obtained.

The reaction is smooth with *p*-dibromobenzene and the product is obtained without the addition of any diluent. With *o* iodotoluene also the reaction is smooth but the iodine atom is in this case replaced by the nitro-group.

With *p*-chlorophenol, cinnamic acid and α-nitronaphthalene, the reaction is not so vigorous but each of them is dissolved in chloroform or carbon tetrachloride so that the reacting mixture could be brought into intimate contact with each other.

Benzoin and hydroquinone are not nitrated but converted into oxidation products.

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Interaction of Iodine Monochloride with Substances Containing the Reactive Methylene Group.

By K. G. Naik and C. C. Shah.

Although the chloro- and bromo-derivatives of substituted malonamides have been extensively prepared and studied (Backes, West and Whiteley, *J. Chem. Soc.*, 1921, **119**, 362 ; West, *ibid*, 1922, **121**, 2196 ; 1924, **125**, 710; 1925, **127**, 748; Naik and Shah, *J. Indian Chem. Soc.*, 1927, **4**, 11), iodo-derivatives of the same are not known. However, di-iodomalonic acid and methyl di-iodomalonate have been prepared by Willstätter (*Ber.*, 1902, **35**, 1377), who describes them as very unstable substances decomposing spontaneously at ordinary temperature.

Moreover, in view of the fact that the chloromalonamides are more stable than the bromomalonamides (West, *loc. cit.*), it was expected that iodomalonamides will be very reactive and will thus form an interesting subject for the study of the effect of the adjoining groups on the two hydrogen atoms of the reactive methylene group, which problem is being tackled in this laboratory for the last several years (Naik, *J. Chem. Soc.*, 1921, **119**, 379 and subsequent papers).

With this end in view, the interaction of iodine monochloride with the following substances was studied :—

(1) Malondipropylamide, (2) malondiheptylamide, (3) malonamide, (4) malondibenzylamide, (5) malondiphenylamide, (6) malondi-*o*-tolylamide, (7) malondi-*p*-tolylamide, (8) malondimethylphenylamide, (9) malondi-α-naphthylamide, (10) malonmonophenylamide, (11) malonmono-*p*-tolylamide, (12) methylmalondiphenylamide, and (13) methylmalondi-*o*-tolylamide.

The use of iodine monochloride as an iodinating agent is well known (Schützenberger, *Z. Chem. Pharm.*, 1861, **5**, 1; Michael and Norton, *Ber.*, 1878, **11**, 108; Ostermeyer, C, **1884**, 937 ; Wheeler and Liddle, *Amer. Chem. J.*, 1909, **42**. 441; C., **1910**, **I**, 528; Willgerodt and Arnold, *Ber.*, 1901, **34**, 3344; Cofman, *Gazzetta*, 1920, II, **50**, 296; C., **1921**, **I**, 943) specially in the case of aromatic compounds. It was expected that here also, iodo-derivatives of the substituted malonamides will be obtained. But contrary to our expectations we only obtained chloro-derivatives many of which have already been prepared by Naik and Shah (*loc. cit.*).

Of the compounds investigated, in the case of (1), (2), (3), (4), (6), (7) and (11), the reactive methylene group was converted into $-CCl_2$ without the halogenation of the nucleus, while in the case of (9), the nucleus was also attacked and $CCl_2(CO{\cdot}NHC_{10}H_6Cl)_2$ was obtained. In the case of (8) and (10), only one hydrogen atom of the methylene group was attacked with the formation of the—CHCl group, the nuclei in the case of (8) remaining unaffected. In the case of (12) and (13), having only one available hydrogen in the methylene group, $MeCCl(CO.NHC_6H_4Cl)_2$ and $MeCCl(CO.NHC_7H_6Cl)_2$ were formed.

Malon-diphenylamide (5) forms a curious exception, for in this case the methylene group remains intact, the nuclei only being halogenated, giving rise to $CH_2(CO{\cdot}NHC_6H_4Cl)_2$. The same compound was obtained by Naik and Trivedi (*J. Indian Chem. Soc.*, 1930, **7**, 239) by the action of selenium tetrachloride on the same substance.

The method for differentiating the chlorine atoms in the methylene group from those in the nucleus was the same as the one adopted by Naik and Shah (*loc. cit.*).

Experimental.

The amide (1 mol.) was treated with iodine monochloride (4 mols.) in presence of chloroform. After allowing the reaction mixture to remain at ordinary temperature (30°) for twentyfour hours, it was refluxed on a water-bath for three hours. The chloroform solution was then shaken with 10 per cent. sodium thiosulphate to remove free iodine and after separation from the aqueous layer was evaporated to dryness. The resulting solid was crystallised from a suitable solvent. In the case of dichloromalonamide, nothing was recovered from the chloroform solution, so the white mass adhering to the flask was extracted with water, and was boiled till all the iodine volatilised; the solution was then concentrated when the product separated.

In this way, malon-dipropylamide gave rise to dichloromalondipropylamide (Naik and Shah), malondiheptylamide to dichloromalondiheptylamide (Naik and Trivedi), malonamide to dichloromalonamide (Backes, West and Whiteley), malondibenzylamide to dichloromalondibenzylamide (N. and S.), malondiphenylamide to malondichlorophenylamide (N. and T.), malondi-*o*-tolylamide to dichlo-

romalondi-*o*-tolylamide (N. and S.), malondi-*p*-tolylamide to dichloromalondi-*p*-tolylamide (N. and S.), malondimethylphenylamide to monochloromalondimethylphenylamide (N. and S.), and malonmono-*p*-tolylamide to dichloromalonmono-*p*-tolylamide (N. and S.).

Dichloromalondichloro-α-naphthylamide was obtained from one g. of the amide and 4 g. of iodine monochloride. It was recrystallised from benzene as white needles, m.p. 191°. It is fairly soluble in alcohol, benzene and chloroform but slightly so in petroleum. (Found: Cl, 28·71; Cl(malonyl), 14·44. $C_{23}H_{14}O_2N_2Cl_4$ requires Cl, 28·92; Cl (malonyl), 14·46 per cent.).

Monochloromalonmonochlorophenylamide.—One g. of the amide and 6 g. of iodine monochloride in 25 c.c. of chloroform were taken. The white substance was crystallised from benzene, m.p. 152°.

It is easily soluble in alcohol, benzene, chloroform and acetic acid but almost insoluble in light petroleum. (Found: Cl, 28·35; Cl (malonyl), 14·80. $C_9H_8O_2N_2Cl_2$ requires Cl, 28·86; Cl (malonyl), 14·43 per cent.).

Methylchloromalondichlorophenylamide.—One g. of methylmalondiphenylamide and 4 g. of iodine monochloride were used. The product separated from benzene; m.p. 164°. It is very soluble in chloroform, acetone and ether but less so in benzene and alcohol. (Found: Cl, 28·31; Cl (malonyl), 9·74. $C_{16}H_{13}O_2N_2Cl_3$ requires Cl, 28·67; Cl (malonyl). 9·55 per cent.).

Methylchloromalondichloro-o-tolylamide was obtained by the interaction of 3·5 g. iodine monochloride with 1 g. methylmalondi-*o*-tolylamide in 25 c.c. chloroform. It crystallises in fine needles from benzene and melts at 184°. It is very soluble in acetone but less so in benzene, alcohol and chloroform, and insoluble in petroleum. (Found: Cl, 26·74; Cl (malonyl), 9·31. $C_{18}H_{17}O_2N_2Cl_3$ requires Cl, 26·62; Cl (malonyl), 8·88 per cent.).

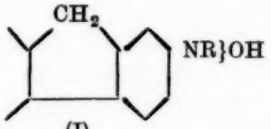
The authors take this opportunity to express their gratitude to the Government of His Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work. One of the authors (C.C.S.) also records his gratitude to His Highness the Maharaja of Rajpipla, for a scholarship which has enabled him to carry out this piece of research.

CHEMISTRY DEPARTMENT, BARODA COLLEGE. *Received October* 24, 1929.

Some Indenoquinoline Derivatives.

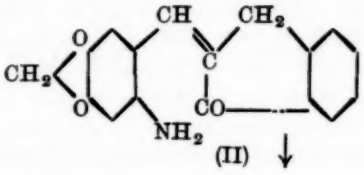
By Gurcharan Singh and Jnanendra Nath Rây.

At the present time the lower homologue of benzene (C_5H_5) or its derivatives have not been prepared. Armit and Robinson (*J. Chem. Soc.*, 1922, **121**, 827) came to the conclusion that this type of bodies can be derived from the decomposition of a quaternary hydroxide containing the group (I) or an analogous structure.

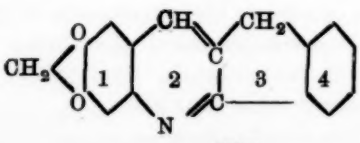


(I)

Types analogous to (I) can be readily prepared from the methohydroxides derived from indenoquinolines. One of these has already received the attention of Armit and Robinson (*loc. cit.*) and accordingly these were chosen for examination in the first place. Armit and Robinson condensed aminopiperonal and α-hydrindone in cold alcoholic solution in presence of potassium hydroxide but they got an unexpected result. The product was the unsaturated ketone (II) which, however, was changed into the quinoline (III) on treatment with acetic acid.



(II) ↓



(III)

The obvious difficulty of extending this reaction led to its abandonment, and they looked for in other directions for the realisation of the structure $(CH)_5$ in association with other ring-systems. In the present paper, we found reasons, which would be stated later on, why it is so very difficult to deal with compounds of this character. Moreover, aminoaldehydes are rather tedious and difficult to prepare. It seemed to us that if a suitable way is found to effect a condensation between an *o*-nitroaldehyde and hydrindones the products are more likely to lead to the desired quinolines on reduction. But the obvious difficulty is that the only method employed hitherto for effecting a condensation between a nitroaldehyde and a reactive methylene group is by the employment of alkali or ethoxides of alkali metals. But the very nature of the condensing agent restricts its applicability and therefore as a preliminary to the main investigation we turned our attention to the finding out of a suitable means of bringing about these condensations. Our object was to try the reactions between a compound containing $-CO\cdot CH_2$-group and various *o*-nitroaldehydes. Alkali was first chosen as a condensing agent. Since the hydrindones are difficult to prepare, therefore, we decided in the first place to employ desoxybenzoin, $Ph\cdot CO\cdot CH_2\cdot Ph$ (a substance easily available and having the same reactive grouping) as a trial substance.

The condensation of desoxybenzoin with *o*-nitrobenzaldehyde in presence of alkali as a condensing agent gave two products having melting points 110° and 210°, respectively. To the first we could not assign any structure, but the second compound (IV) is formed according to the following equation:

$$Ph\cdot CO\cdot CH_2\cdot Ph + C_6H_4\begin{cases}NO_2\\CHO\end{cases} = C_6H_4\begin{cases}NO_2\\CH=C\cdot Ph\end{cases}\!\!\begin{matrix}\\|\\CO\cdot Ph\end{matrix}$$

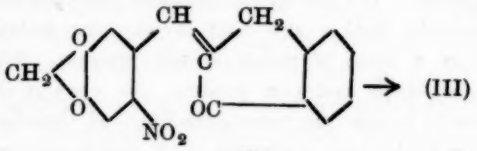
(IV)

Although the isolation of two products, one of uncertain constitution, indicated that alkali is hardly a suitable reagent yet we attempted to use the alkali in the condensation of hydrindone and *o*-nitrobenzaldehyde, but this failed, and after many fruitless trials with different agents it was ultimately found that this condensation takes place in presence of acetic anhydride.

α-Hydrindone, methylenedioxyhydrindone and dimethoxyhydrindone were thus condensed with *o*-nitrobenzaldehyde, nitropiperonal

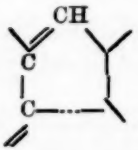
and nitroveratric aldehyde to give the corresponding *o*-nitro-$\alpha\beta$-unsaturated ketones.

The reduction of the nitroarylidenehydrindones presented considerable difficulty. This at first seemed to be of a puzzling character, seeing that Armit and Robinson had already, although not satisfactorily, reduced (V) to (III).



(V)

We employed sodium sulphide as a most likely reducing agent but we were unfortunately not able to isolate any pure product. This we later found out to be due to the fact that in alkaline medium (as well as in acid medium) the quinolines formed immediately underwent oxidation. We are inclined to think that the ring 3 in (III) is the one which is oxidised to the form,



along with probably many other associated products and that is why the isolation of these derivatives of *cyclo*pentamethine is so very difficult. Next we turned our attention to the employment of zinc dust and acetic acid for these reductions, but here an unexpected difficulty presented itself. With the progress of the reduction brilliant fluorescence appeared in the solution, but from the reaction product nothing crystalline could be isolated. This we did not understand for a while but subsequently it was found that if air was rigorously excluded from the reaction vessel and particular care was taken to free the zinc dust from zinc oxide, these fluorescence ceased to appear. The desired indenoquinolines could then be isolated, if the whole of the operation be conducted in an atmosphere of hydrogen and to the total exclusion of air. This appearance of fluorescence obviously was due to the rapid oxidation of the ring 3 of (III) to the pentamethine derivative by air.

Our objective was to isolate these pentamethine derivatives, therefore we allowed, for a time, the air to play the rôle of an oxidising agent with the hope that it would be possible to isolate our desired pentamethines.

The pentamethines are more likely to be fluorescent than indenoquinolines. This is why with the introduction of air intense fluorescence appears, but the action probably does not stop at this stage and proceeds further and that is why the isolation of the pentamethine in a state of purity, is not possible. After many attempts to isolate such oxidation product, we gave up the project and decided first to isolate the indenoquinoline and therefore carried on the reduction to the total exclusion of air, and then proceed on to the oxidation of these to the pentamethine derivatives, as it was thought by starting from the pure substances we were more likely to isolate the pentamethine derivatives. Therefore in the experimental part, we describe the isolation of these indenoquinolines and reserve, for the time being, the conversion of these indenoquinolines to the pentamethines.

Experimental.

The following modification worked better in the preparation of 6-nitroveratric aldehyde (*cf.* Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3412) and nitropiperonal.

Veratric aldehyde (15 g.) was gradually introduced into nitric acid (30 g., *d* 1·42) kept at 5-10°, with stirring. The product was diluted with ice-water and the yellow crystals collected, washed with ice-water and recrystallised from alcohol; m.p. 132-33° ; yield 70 per cent.

Piperonal (15 g.) dissolved in 8 c.c. of acetic acid was gradually added to nitric acid (16 c.c., *d* 1·5) kept below 6°. A little more of acetic acid was found to hinder the nitration. When all of the piperonal was added, the product was allowed to remain at the same temperature for about fifteen minutes, then poured on to water, the yellow crystals collected and recrystallised from methyl alcohol, m.p. 95°.

Condensation of Desoxybenzoin with o-Nitrobenzaldehyde: Formation of (IV).—Desoxybenzoin (19·6 g.) and o-nitrobenzaldehyde (15·1 g. dissolved in 100 c.c. of alcohol) were mixed with 1 c.c. (50 per cent.) potassium hydroxide solution. It was then refluxed on the water-bath for an hour, cooled and poured on to water, and the solid product collected. It consists of two substances one of which is

readily soluble in hot alcohol and the other insoluble. The soluble portion crystallises in long, yellow needles melting at 110°. (Found: N, 6·1 per cent. M.W. 258). As these results do not agree with that of any of the expected compounds, we could not assign any structure to it.

The insoluble portion was dried and crystallised from benzene. This compound melts at 210° and the crystals are bright yellow in colour. (Found: N, 4·5. $C_{21}H_{15}O_3N$ requires N, 4·3 per cent.). Attempts to reduce this product failed.

Condensation of α-Hydrindone with o-Nitrobenzaldehyde: Formation of 2'-Nitrobenzylidene-α-hydrindone.—Hydrindone (13·2 g.), *o*-nitrobenzaldehyde (15·1 g.) and acetic anhydride (40 c.c.) were heated for two hours under reflux. The product solidified in contact with water which was collected and best crystallised from glacial acetic acid in pale needles, m.p. 167°. (Found: N, 5·4. $C_{16}H_{11}O_3N$ requires N, 5·3 per cent.). The compound is sparingly soluble in hot alcohol but is readily soluble in hot acetic acid.

Reduction of the above Compound: Formation of Indenoquinoline.—The nitrobenzylidenehydrindone was heated with zinc dust and acetic acid for an hour and then filtered while hot. On addition of water the quinoline separated out as a chalky precipitate, which was collected and dried. This product was very difficult to crystallise. The compound was dissolved in alcohol, to which a few drops of concentrated hydrochloric acid were added. This on dilution with a little water deposited pale yellow crystals, m.p. 170-75°. The hydrochloride is sparingly soluble in aqueous alcohol. (Found: N, 5·8. $C_{16}H_{11}N,HCl$ requires N, 5·52 per cent.).

In this case no fluorescence appears, and probably the reduced product here is not so easily oxidisable by air.

Condensation of α-Hydrindone with 6-Nitropiperonal: Formation of 6'-Nitro-3':4'-methylenedioxybenzylidenehydrindone.—Hydrindone (13·2 g.), 6-nitropiperonal (19·5 g.) and acetic anhydride (40 c.c.) were condensed as before. The product was poured on to water; on cooling, the yellow crystals were collected, and recrystallised from glacial acetic acid in yellow prisms, m.p. 178°; yield, 6 g. (Found: C, 65·8; H, 3·7; N, 4·7. $C_{17}H_{11}O_5N$ requires C, 66·0; H, 3·5; N, 4·5 per cent.). The substance is sparingly soluble in hot alcohol but is quite soluble in glacial acetic acid. This compound has been prepared before by Armit and Robinson (*J. Chem. Soc.*, 1922, **125**, 827) who give m.p. 182°.

Reduction of Nitropiperonylidenehydrindone: Formation of 6′: 7′-Methylenedioxy-2: 3-indeno-1: 2-quinoline Hydrochloride (III).—This compound was obtained by heating 6-nitropiperonylidene hydrindone with zinc dust and acetic acid. The solution first developed an orange-red colour which with the progress of the reaction changed to light orange. Nitropiperonylidenehydrindone is first reduced to the amino-compound which further is quickly converted into the quinoline derivative. This experiment presented considerable difficulty as it had to be performed in complete absence of air and the whole operation done in the presence of hydrogen.

Zinc dust and acetic acid were first gently boiled for a few minutes to destroy any zinc oxide present in the zinc, and also to chase all the air from the reaction vessel. Then the nitro-compound was gradually added with occasional shaking and the heating continued till the reduction was complete. Near the end of the reaction the colour of the solution became lighter (about $1\frac{1}{2}$ hour). Then the mixture was quickly filtered in an atmosphere of hydrogen into a flask containing ice, and kept cold in a freezing bath, through which hydrogen was constantly passing. The filtrate was completely neutralised with a cold solution of strong sodium hydroxide kept in an atmosphere of hydrogen. The quinoline which separated out was extracted by ether in an atmosphere of hydrogen, the ethereal solution filtered into a distillation flask from which air has been expelled by saturating it with ether vapour. The dried ethereal solution was distilled, the oily residue dissolved in alcohol and the hydrochloride formed by adding concentrated hydrochloric acid which deposited brick-red crystals on dilution with a little water. The hydrochlorides of this series are curiously soluble in alcohol but almost insoluble in aqueous alcohol. The compound shrinks at 194° and melts with decomposition at 197°. (Found: N, 4·9. $C_{17}H_{11}O_2N$, HCl requires N, 4·7 per cent.).

Condensation of α-Hydrindone with Nitroveratric Aldehyde: Formation of 6′-Nitro-3′: 4′-dimethoxybenzylidene-α-hydrindone.—α-Hydrindone (13·2 g.), nitroveratric aldehyde (21·1 g.) and acetic anhydride (40 c.c.) were condensed as before. On cooling the product was poured on to water and the yellow crystals separating out collected and crystallised from glacial acetic acid. (Found: N, 4·9. $C_{18}H_{15}O_5N$ requires N, 4·3 per cent.). This compound melts at 210° and crystallises in yellow needles.

Condensation of Methylenedioxyhydrindone and o*-Nitrobenzaldehyde: Formation of 6′-Nitrobenzylidene-3:4-methylenedioxyhydrindone.*—3:4-Methylenedioxyhydrindone (17·6 g.), *o*-nitrobenzaldehyde (15·1 g.) and acetic anhydride (40 c.c.) were heated under reflux for two hours. On cooling the product was poured on to water and allowed to remain for some time. The solid which separated out was collected and crystallised from glacial acetic acid. (Found: N, 4·6. $C_{17}H_{11}O_5N$ requires N, 4·5 per cent.); yield, 8 g. The compound melts at 212° and crystallises in yellow needles.

Reduction of the above Compound: Formation of Methylenedioxyindenoquinoline.— 6′-Nitrobenzylidene - 3:4 - methylenedioxyhydrindone, zinc dust and acetic acid were heated for an hour. The solution first showed a deep uranium-blue fluorescence which practically disappeared with the progress of the reaction. The solution was then quickly filtered, neutralised with caustic soda; the precipitate of the free base collected, dried and crystallised from a mixture of benzene and petroleum ether. (Found: N, 5·6. $C_{17}H_{11}O_2N$ requires N, 5·4 per cent.). The compound shrinks at 195° and melts at 202°.

Condensation of Methylenedioxyhydrindone with Nitropiperonal: Formation of 6′-Nitro-3′:4′-methylenedioxybenzylidene-3:4-methylenedioxyhydrindone.—3:4-Methylenedioxyhydrindone (17·6 g.), nitropiperonal (19·5 g.) and acetic anhydride (40 c.c.) were condensed as before. The product on cooling was poured on to water, the solid collected and crystallised from glacial acetic acid. (Found: N, 4·1. $C_{18}H_{11}O_7N$ requires N, 4·0 per cent.). The compound crystallises in deep yellow needles melting at 232°; yield, 12 g.

Reduction of the above Compound: Formation of Dimethylenedioxyindenoquinoline.—6′-Nitropiperonylidene - 3:4 - methylenedioxyhydrindone was added to acetic acid and zinc dust, which had already been boiling for some time. After 1½ hour the solution was filtered into a flask containing ice and kept cool from outside, and through which hydrogen was constantly passing. The filtrate was then completely neutralised with a cold solution of strong sodium hydroxide kept in an atmosphere of hydrogen. The quinoline which separated out was extracted with ether in an atmosphere of hydrogen. The ethereal solution on distillation furnished the quinoline as a pale white crystalline mass, m.p. 283°. (Found: N, 4·7. $C_{18}H_{11}O_4N$ requires N, 4·6 per cent.).

Condensation of Methylenedioxyhydrindone and Nitroveratric Aldehyde: Formation of 6′-Nitro-3′:4′-dimethoxybenzylidene-3:4-methylenedioxyhydrindone.—3:4-Methylenedioxyhydrindone (17·6 g.), nitroveratric aldehyde (21·1 g.) and acetic anhydride (40 c.c.) were condensed as before. On cooling, the product was poured on to water, the yellow needles collected and crystallised from glacial acetic acid ; m.p. 250°. (Found: N, 3·9 $C_{19}H_{15}O_7N$ requires N, 3·8 per cent.).

Reduction of the above Compound: Formation of Dimethoxymethylenedioxyindenoquinoline.—6′-Nitro-3′:4′-dimethoxybenzylidene-3:4-methylenedioxyhydrindone was added to a mixture of zinc dust and acetic acid which had been kept boiling. The solution develops a deep orange colour in the beginning which changes to pale yellow with the progress of the reaction. After 1½ hour the solution was quickly filtered in an atmosphere of hydrogen. The filtrate was then neutralised with an ice-cold solution of strong caustic soda in an atmosphere of hydrogen. The quinoline which separated out was extracted with ether, the ether distilled off, care being teken to exclude air. The oily mass left behind was dissolved in alcohol, to which concentrated hydrochloric acid was added, and the hydrochloride crystallised out in yellow needles on addition of water. The compound shrinks at 255° and melts with decomposition at 257°. (Found: N, 4·1. $C_{19}H_{15}O_4N$, HCl requires N, 3·9 per cent.).

Condensation of 3:4-Dimethoxyhydrindone with o-Nitrobenzaldehyde: Formation of 6′-Nitrobenzylidene-3:4-dimethoxyhydrindone.—3:4-Dimethoxyhydrindone (19·2 g.), *o*-nitrobenzaldehyde (15·1 g.) and acetic anhydride (40 c.c.) were condensed as before. The product was crystallised from glacial acetic acid in lemon yellow needles, m.p. 188°; yield, 12 g. (Found: N, 4·5. $C_{19}H_{15}O_5N$ requires N, 4·3 per cent.).

Reduction of the above Compound: Formation of Dimethoxyindenoquinoline Hydrochloride.—The nitrobenzylidenedimethoxyhydrindone was reduced as before. The solution first showed orange-yellow colour which almost disappeared near the end of the reaction. After heating for 1½ hour the solution was filtered quickly in an atmosphere of hydrogen and the filtrate neutralized with a strong solution of caustic soda. The quinoline was extracted with ether; the ethereal solution showed a very pale bluish-yellow fluorescence. The free base left behind as an oily mass was converted into its hydrochloride by taking it an alcohol, adding concentrated hydro-

chloric acid and crystallising by addition of water. The hydrochloride came out in pale yellow crystals, which shrink at 231° and melt with decomposition at 232°. (Found: Cl, 10·6; N, 4·67. $C_{18}H_{15}O_2N$, HCl requires Cl, 11·3; N, 4·47 per cent.).

Condensation of 3:4-*Dimethoxyhydrindone with Nitropiperonal: Formation of* 6′-*Nitro*-3′:4′-*methylenedioxybenzylidene*-3:4-*dimethoxyhydrindone.*—3:4-Dimethoxyhydrindone (19·2 g.), nitropiperonal (19·5 g.) and acetic anhydride (40 c.c.) were condensed as before, and the product crystallised from glacial acetic acid in yellow needles; m.p. 232°. (Found: N, 4·0. $C_{19}H_{15}O_7N$ requires N, 3·8 per cent.).

Reduction of the above Compound: Formation of Methylenedioxydimethoxyindenoquinoline.—Nitropiperonylidenedimethoxyhydrindone was reduced as before. The solution first showed a deep red colour which became lighter with the progress of the reaction. After the heating had been continued for 1½ hour the solution was treated as in the other cases. The quinoline obtained as an oily mass was converted into its hydrochloride, which crystallised in yellow crystals on dilution with water, m.p. 270° with decomp. (Found: N, 3·9. $C_{19}H_{15}O_4N$, HCl requires N, 3·9 per cent.).

Condensation of Dimethoxyhydrindone with Nitroveratric Aldehyde: Formation of 6′-*Nitro*-3′:4′-*dimethoxybenzylidene*-3:4-*dimethoxyhydrindone.*—3:4-Dimethoxyhydrindone (19·2 g.), nitroveratric aldehyde (21·1 g.) and acetic anhydride (40 c.c.) were condensed as before. The product crystallised in yellow needles from glacial acetic acid; m.p. 237°; yield, 14 g. (Found: N, 4·0. $C_{20}H_{19}O_7N$ requires N, 3·64 per cent.).

Reduction of the above Compound: Formation of Tetramethoxyindenoquinoline. — Nitrodimethoxybenzylidenedimethoxyhydrindone was reduced by zinc dust and acetic acid in the usual manner. The quinoline separated as an oily mass after the usual treatment, was dissolved in alcohol and converted into the hydrochloride. This crystallises in yellow needles on dilution, shrinking at 234° and melting with decomposition at 235°. (Found: N, 3·99. $C_{20}H_{19}O_4N$, HCl requires N, 3·75 per cent.).

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Stability of Unsaturated Compounds in Presence of Catalysts.

By M. N. Goswami.

The unstability of acetylene, ethylene, propylene and trimethylethylene in presence of nickel or copper at 200° has been exhaustively shown by Sabatier and Senderens (*Bull. Soc. Chim.*, 1899, **21**, 530 ; *Compt. rend.*, 1900, **130**, 250 ; 1902, **134**, 1127) ; they found that under these conditions acetylene spontaneously decomposed with the deposition of carbon and with the formation of various aromatic liquid products and cuprene $n(C_7H_6)_2$. In some experiments on catalysis, a mixture of naphthalene vapour and acetylene was passed over nickel at 200° but surprisingly there was no decomposition ; similar results were obtained with naphthalene and ethylene; benzene with acetylene or ethylene behaved in an identical way. This stability of acetylene and ethylene was evidently due primarily to dilution with benzene or naphthalene. When however phenylethylene (styrolene) was passed over nickel and not the slightest decomposition was observed even at 350°, it became apparent that the stability of the unsaturated linkages might be also due to the influence of contiguous groups. The present work is an attempt to investigate this question. Besides Sabatier and Senderens' work, other researches have been done on the decomposition of acetylene and ethylene and other unsaturated compounds. Thus Moissan and Moureau (*Compt. rend.*, 1896, **122**, 1241) have observed that finely divided platinum decomposes acetylene at 150° spontaneously and there is so much evolution of heat that the metal becomes incandescent. Mailhe in a series of papers has shown the course of decomposition of oleic acid, oleins and other unsaturated glycerides when they are passed over reduced nickel (*Compt. rend.*, 1922, **174**, 873; *Ann. Chim.*, 1922, **17**, 304). But so far no attempt has been made, in such catalytic decompositions, to find out the influence of the contiguous groups, attached to the unsaturated linkages. The stabilising influence of phenyl radicle, as was observed in the case of phenylethylene, was also seen when phenylacetylene was treated in a similar way and

found to remain undecomposed. Eugenol was only partly transformed into *iso*eugenol. Sym.-diphenylethylene was found to be quite stable. Ethyl cinnamate in which the group CH=CH is attached to phenyl and carbethoxy radicles did not suffer any decomposition but the case was otherwise with cinnamic acid, alcohol and aldehyde.

Cinnamic acid decomposed in two ways, normally like formic and acetic acids (Sabatier and Mailhe, *Compt. rend.*, 1911, **152**, 1212).

$$CH_3{\cdot}CO_2H = CH_4 + CO_2$$

and abnormally with the production of benzene, phenylacetylene and diphenylethylene probably according to the following equations:—

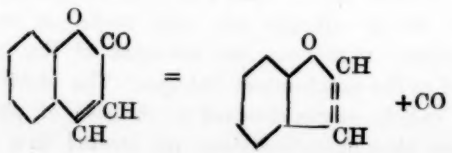
$$Ph{\cdot}CH : CH{\cdot}CO_2H = PhCH : CH_2 + CO_2$$
$$Ph{\cdot}CH : CH{\cdot}CO_2H = PhH + CH{\equiv}CH + CO_2$$
$$Ph{\cdot}CH : CH{\cdot}CO_2H = PhC{\equiv}CH + H_2 + CO_2$$
$$PhCH : CH_2 + PhH = PhCH : CHPh + H_2$$
$$CH{\equiv}CH = C + H_2$$
$$4H_2 + CO_2 = CH_4 + 2H_2O$$

Nearly 90% of the cinnamic acid decomposed and the products consisted of 70% phenylethylene, 10% benzene, 10% phenylacetylene and 10% diphenylethylene. Phenylacetylene did not seem to have been formed from phenylethylene as the latter under the conditions of the experiment was found to be stable. Cinnamic alcohol and aldehyde at 350° decomposed into phenylethylene.

$$Ph{\cdot}CH : CH{\cdot}CH_2OH = PhCH : CH_2 + CH_2O$$
$$PhCH : CH{\cdot}CHO = PhCH : CH_2 + CO$$

These results show that the carbethoxy group like phenyl has stabilising influence on the unsaturated linkage whereas the groups. CO_2H, CHO, CH_2OH cannot protect it.

Experiments with coumarin gave coumarone presumably according to the following equation:—



Ethyl acetoacetate (enolic) decomposed into acetone, carbon dioxide and ethylene. Here it may be noted that although of the two stabilising groups, *viz.*, phenyl and carbethoxy, the latter is present, there is another hydroxyl group which makes the whole system labile and thus hastens the decomposition.

The reaction products were detected and identified. The results so far obtained may be summarised thus:—

(*a*). Phenyl and carbethoxy groups have stabilising influence no unsaturated linkages.

(*b*). The groups CH_2OH, CO_2H and CHO cannot protect the unsaturated bonds. Further experiments in this line are in progress.

Experimental.

Reduced Nickel.—Commercial nickel nitrate was converted into the oxalate; this was heated on the sand-bath when nickel oxide was obtained in a very porous form. It was then reduced at 300° in a current of purified hydrogen.

Experiments with Cinnamic Acid.

Vapours of cinnamic acid were passed over the catalyst at 350° and a product was obtained which on fractionation gave—

Fraction (*a*), b. p. 80-82°, which was identified as benzene.

Fraction (*b*), b. p. 135-142°. It was found to be phenylacetylene as it gave the characteristic reaction with silver nitrate (white ppt.) and with copper sulphate (yellow ppt.) ; when treated with sulphuric acid it gave acetophenone which was identified.

Fraction (*c*), b. p. 146-150°. It was identified to be phenylethylene; it gave a dibromo-derivative, m.p. 74°; the m.p. was not depressed by admixture with a genuine specimen of styrolene dibromide.

Residue.—It was repeatedly washed with hot water and sodium carbonate solution to eliminate cinnamic acid and was then crystallised from alcohol; m.p. 124°; the picrate melted at 237°. (Found: C, 93·58; H, 6·44. $C_{14}H_{12}$ requires C, 93·33; H, 6·66 per cent.).

Hence the substance was diphenylethylene.

Coumarin.—Vapours of coumarin were passed over nickel at 350° and the liquid obtained on fractionation gave primarily a product boiling at 169°, the bromo-derivative of which melted at 88°. These facts point out that the liquid is coumarone.

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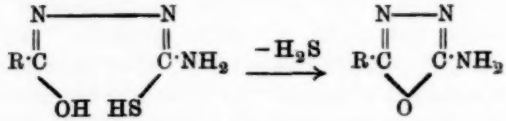
Studies on Oxidation. Part III. Behaviour of Formyl-, Acetyl- and Benzoyl-thiosemicarbazide towards Lead Oxide.

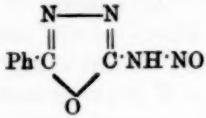
By Satish Chandra De.

In the present communication a few furodiazoles have been described which were obtained by the oxidation of the thiosemicarbazides with lead oxide. In the reaction process hydrogen sulphide was removed from the thiosemicarbazide converting the oxide into a black sulphide. The course of the reaction is represented by the following scheme :—

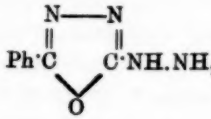


(I)

The formation of a diazonium chloride by the action of nitrous acid on 2-aminofurodiazole and 2-amino-5-methylfurodiazole in hydrochloric acid solution could not be established. 2-Amino-5-phenylfurodiazole in dilute hydrochloric acid solution gave with nitrous acid a nitroso- amine (II),

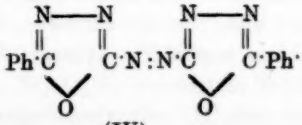


(II)

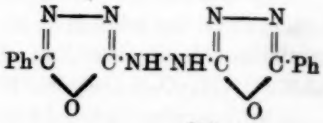


(III).

which, on reduction, was converted into the hydrazine (III). The latter could be isolated as the benzylidene compound. 2-Amino-5-phenylfurodiazole was oxidised with calcium hypochlorite solution to an azo-compound (IV) and the latter was reduced to the hydrazo-compound (V).



(IV).



(V).

Experimental.

2-*Amino*-1:3:4-*furodiazole* (I, R=H).—Formylthiosemicarbazide (10 g. in 400 c.c. of alcohol) was boiled with lead oxide (100 g.) for about 20 hours. The black lead sulphide was filtered off and the filtrate concentrated when a white crystalline solid was obtained. This was crystallised from water in white rectangles, m.p. 155°. (Yield very poor). (Found: N, 49·53. $C_2H_3ON_3$ requires N, 49·41 per cent.). It is soluble in water and alcohol. A solution of the furodiazole in strong hydrochloric acid turned light yellow on the addition of sodium nitrite solution.

2-*Amino*-5-*methyl*-1:3:4-*furodiazole* (I, R=Me).—Acetylthiosemicarbazide (10 g. in 400 c.c. of alcohol) was boiled with lead oxide (80 g.) for 24 hours. The filtrate from the lead sulphide on concentration deposited a white solid which was crystallised from a mixture of water and alcohol in white rectangles, m.p. 183°. (Found: N, 42·56. $C_3H_5ON_3$ requires N, 42·42 per cent.). It is soluble in hot water and in alcohol. Its solution in hydrochloric acid turned yellow with a solution of sodium nitrite.

The *acetyl* derivative crystallised from alcohol in yellowish-white needles, m.p. 180°. (Found: N, 29·69. $C_5H_7O_2N_3$ requires N, 29·79 per cent.).

2-*Amino*-5-*phenyl*-1:3:4-*furodiazole* (I, R=Ph).—Benzoylthiosemicarbazide (10 g. in 400 c.c. of alcohol) was boiled with lead oxide (60 g.) for 24 hours. The solution after the removal of lead sulphide was concentrated when white prismatic crystals were obtained in good yield. Recrystallised from alcohol it melts at 245° (decomp.). (Found: N, 26·22. $C_8H_7ON_3$ requires N, 26·09 per cent.). It is insoluble in cold and slightly soluble in hot water and readily soluble in hot alcohol. From hot dilute hydrochloric acid solution the hydrochloride of the base separated out which decomposes at 175-6°.

2-*Acetylamino*-5-*phenyl*-1:3:4-*furodiazole* was crystallised from water in white needles, m.p. 223°. (Found: N, 20·80. $C_{10}H_9O_2N_3$ requires N, 20·69 per cent.).

2-*Benzoylamino*-5-*phenyl*-1:3:4-*furodiazole*.—It was prepared by boiling a pyridine solution of the diazole with benzoyl chloride. It crystallised from alcohol in white needles, m.p. 203°. (Found: N, 15·97. $C_{15}H_{11}O_2N_3$ requires N, 15·85 per cent.).

2-*Nitrosoamino*-5-*phenyl*-1:3:4-*furodiazole* (II).—To a suspension of aminophenylfurodiazole hydrochloride in dilute hydrochloric acid,

an aqueous solution of sodium nitrite was slowly added with continuous stirring. A yellowish-white mass soluble in caustic alkalis was thus obtained. It separated from alcohol in light yellow crystals which turned black at 103°. (Found: N, 29·35. $C_8H_6O_2N_4$ requires N, 29·47 per cent.). It is insoluble in water, easily soluble in ether and in hot alcohol.

2-Benzylidenehydrazino-5-phenyl-1:3:4-furodiazole.—The above nitroso-amine was suspended in water to which zinc dust was added. This was then cooled and treated with a dilute acetic acid solution. The mixture was allowed to stand for 6 hours with frequent shaking when the nitroso-compound gradually went into solution. The solution was filtered from the zinc dust and shaken up with benzaldehyde. A white solid was thus obtained which was pressed on a porous plate to remove the adhering aldehyde and then crystallised from alcohol in white needles, m.p. 243° (decomp.). (Found: N, 21·35. $C_{15}H_{12}ON_4$ requires N, 21·21 per cent.).

It is insoluble in water, slightly soluble in cold and readily soluble in hot alcohol. When the benzylidene compound was boiled with dilute hydrochloric acid for 10 minutes, smell of benzaldehyde was noticed which was removed by passing steam. The clear solution was then evaporated until a crystalline solid was obtained. This was filtered, washed with alcohol and crystallised from hot water, m.p. 208°. This is the hydrochloride of a base, the latter being obtained by treating an aqueous solution of the hydrochloride with ammonia. The white precipitate was crystallised from aqueous alcohol, m.p. 152°. On analysis it gave 47·55% nitrogen. It is not the expected hydrazinofurodiazole but some other compound.

5:5′-Diphenyl-2:2′-azo-1:3:4-furodiazole (IV).—A solution of 2-amino-1:3:4-furodiazole or its 5-methyl derivative turns yellow on treatment with calcium hypochlorite solution, probably due to the formation of the corresponding azo-compound. In the case of the phenyl derivative the azo-compound was isolated as follows: An alcoholic solution of aminophenylfurodiazole was gently warmed with an excess of a concentrated aqueous solution of calcium hypochlorite. The yellow precipitate thus obtained was washed successively with water and alcohol and was crystallised from nitrobenzene as an orange, crystalline powder, m.p. 329-30°. (Found: N, 26·54. $C_{16}H_{10}O_2N_6$ requires N, 26·42 per cent.). It is insoluble in water, alcohol and ether; slightly soluble in hot acetic acid. When the alcoholic suspension of the azo-compound was allowed to stand over-

night with an alcoholic solution of ammonium sulphide a colourless precipitate of the hydrazo-compound (V) was obtained which melted at 233° and turned reddish-yellow with calcium hypochlorite solution.

My thanks are due to Prof. J. C. Ghosh and Dr. P. C. Guha for their kind interest and encouragement during the progress of this investigation.

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Mercuration of Compounds Containing the Reactive Methylene Group.

By K. G. Naik and C. C. Shah.

The mercuration of the substituted amides of malonic acid was undertaken with a view to study the change in the stability of the carbon-mercury linkage in these compounds and thus throw, if possible, some light on the effect of the adjoining groups on the reactivity of the two hydrogen atoms of a methylene group situated between two negative groups, which has been the subject of investigation by Naik and his collaborators (Naik, *J. Chem. Soc.*, 1921, **119**, 379 and subsequent papers).

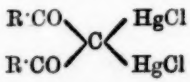
We have employed the method of Neogi and Chatterjee (*J. Indian Chem. Soc.*, 1928, **5**, 221), the mercurating agent being mercuric chloride in presence of sodium bicarbonate and glycerol. It may be that at first an oxychloride of mercury is formed, which subsequently reacts with the organic compounds giving rise to a mercurated product, thus:—

$$HgCl_2 + NaHCO_3 = Hg(OH)Cl + NaCl + CO_2$$
$$R{\cdot}H + Hg(OH)Cl = R{\cdot}HgCl + H_2O.$$

The following compounds were mercurated by this method:—(1) Malonamide, (2) malondimethylamide, (3) malondiethylamide, (4) malondipropylamide, (5) malondi-*n*-butylamide, (6) malondi*iso*butylamide, (7) malondi*iso*amylamide, (8) malondiamylamide, (9) malondiheptylamide, and (10) ethyl malonate.

Of these (7) and (8) were prepared for the first time. Only the alkylamides of malonic acid were selected for the present purpose, in order to avoid the complications that may occur by the entrance of mercury in the nuclei of arylamides.

All the substances enumerated above react with mercuric chloride under the experimental conditions yielding products having the general formula,



where R = ethoxy-, amino-, methylamino-, etc. group.

This constitution has been assigned to the compounds from the following considerations—

(*i*) The mercury has not entered the aliphatic part of the amido-group (−NHR) because—

(*a*) no example seems to have been recorded in literature of mercury having thus substituted a hydrogen atom of an aliphatic compounds ;

(*b*) malonamide, which contains no such aliphatic part, forms a similar mercury derivative;

(*c*) the mercury derivatives of aliphatic compounds are not easily decomposed by potassium iodide and hydrochloric acid, while dichloromercurimalondiheptylamide, obtained during the course of this work, is attacked by these reagents giving the original amide.

(*ii*) The mercury atom has not replaced the *N*-hydrogen atom, for

(*a*) malonic ester which contains no such hydrogen atom forms a similar compound with mercuric chloride ;

(*b*) a study of the known mercurated *substituted* amides shows that the hydrogen attached to nitrogen can be substituted by mercury under exceptional conditions. Acetanilide on fusion with mercuric oxide forms *N*-mercuri-bis-acetanilide (Oppenheim and Paaff, *Ber.*, 1874, **7**, 624 ; Wheeler, *Amer. Chem. J.*, 1896, **18**, 696 ; Pesci, *Gazzetta*, 1897, I, **27**, 568), though a boiling solution of acetanilide gives *p*-acetaminophenylmercuric acetate (Pesci, *Z. anorg. Chem.*, 1897, **15**, 222 ; Dimroth, *Ber.*, 1902, **35**, 2037). Similarly *p*-acetoxymercuri-*o*-acetotoluidide is formed by refluxing *o*-acetotoluidide with mercuric acetate in water (Schrauth, Schoeller and Rother, *Ber.*, 1912, **45**, 2812) while no *N*-mercury-derivative of the same seems to have been reported. Similar results are obtained with *m*- and *p*-acetotoluidides ;

(*c*) the *N*-Hg-compounds behave as weak bases and a solution of mercuri-acetamide can be titrated with hydrochloric acid using methyl orange as indicator (Ley and Kissel, *Ber.*, 1899, **32**, 1357), while the products obtained here are decomposed rather slowly.

(*iii*) The mercury is directly attached to the methylene carbon atom, for—

(*a*) dichloromercurimalonamide gives dibromomalonamide on treatment with bromine ;

(*b*) the properties and behaviour of the products obtained is the same as those of compounds having mercury attached to the carbon in α-position to a keto-group, as is shown below.

The stability of the carbon-mercury bond varies over a very wide range. Thus, in contrast to some of the mercarbides which remain unchanged even after prolonged boiling with fuming hydrochloric acid (Hofmann, *Ber.*, 1898, **31**, 1905 ; 1900, **33**, 1336), substances having a mercury atom attached to a carbon atom in α-position to a keto-group, lose it on treatment with 0·25*N*-hydrochloric acid (Dimroth, *Ber.*, 1902, **35**, 2870).

Ethyl dichloromercurimalonate $(HgCl)_2 : C : (CO_2Et)_2$, which was also prepared by Biilmann (*Ber.*, 1902, **35**, 2580), on treatment with hot concentrated hydrochloric acid, liberates mercuric chloride and forms ethyl monochloromercurimalonate, thus:

$$(HgCl)_2 : C : (CO_2Et)_2 + HCl = HgCl \cdot CH : (CO_2Et) + HgCl_2.$$

It is rather curious to observe that the second mercury atom in the same position is not removed simultaneously. This behaviour is not, however, quite abnormal, for bromomercuriacetic acid, $BrHg \cdot CH_2 \cdot CO_2H$, which contains a mercury atom attached to a carbon atom in α-position to a keto group, is not decomposed by acids (Hofmann and Sand, *Ber.*, 1900, **33**, 1346). In the case of dichloromercurimalondiheptylamide, on the other hand, both the chloromercuri-groups are removed by the action of hydrochloric acid.

It has also been possible to obtain ethyl monochloromercurimalonate by the action of *cold* aqueous potassium iodide on the dichloromercuri-ester, though both the chloromercuri-groups are removed by the action of *hot* potassium iodide solution. Potassium iodide reacts with organo-mercury compounds of the type R·HgX in three different ways: (*i*) it may give rise to compounds of the type R·HgR (Whitmore, *J. Amer. Chem. Soc.*, 1919, **41**, 1850); (*ii*) it may form an iodomercuri-compound, R·HgI (Volhard, *Annalen*, 1892, **267**, 172), or (*iii*) it may bring about a complete splitting up of the carbon-mercury linkage with the liberation of one equivalent of alkali for each carbon-mercury linkage, thus:

$$R \cdot HgX + KI + H_2O = R \cdot H + HgXI + KOH.$$

All compounds having mercury substituted for the hydrogen atoms in the grouping, $-CO \cdot CH_2 \cdot CO-$, $-CO \cdot CH_2 \cdot CN$, etc., behave in the above manner (Biilmann, *Ber.*, 1902, **35**, 2580 ; Biil-

mann and Witt, *Ber.*, 1909, **42**, 1070 ; Petterson, *J. pr. Chem.*, 1912, *ii*, **86**, 464). Dichloromercurimalondiheptylamide is also decomposed by potassium iodide, with the liberation of two equivalents of alkali.

The substances containing mercury in the reactive methylene group are unusually reactive towards hydrogen sulphide, immediately giving mercuric sulphide (Biilmann, *loc. cit.* ; Biilmann and Witt, *loc. cit.* ; Lippmann, *Z. Chem.*, 1869, *ii*, **5**, 29 ; Oppenheim, *Ber.*, 1877, **10**, 701 ; Behrend, *Z. physikal. Chem.*, 1893, **11**, 478 ; Hofmann, *Ber.*, 1898, **31**, 2215 ; Ley, *Ber.*, 1900, **33**, 1014 ; Michael, *Ber.*, 1905, **38**, 2090) ; ethyl dichloromercurimalonate instantaneously gives a black precipitate of mercuric sulphide on treatment with hydrogen sulphide.

Sodium thiosulphate is the most general reagent used to bring about a change from the organo-mercury compounds of the type R· HgX to compounds of the type R_2:Hg (Pesci, *Gazzetta*, 1899, I, **29**, 394 ; Dimroth, *Ber.*, 1908, **35**, 2041 ; Kharasch and Piccard, *J. Amer. Chem. Soc.*, 1920, **42**, 1861 ; Whitmore and Middleton, *ibid*, 1921, **43**, 622, etc.). However, when ethyl dichloromercurimalonate was dissolved in concentrated sodium thiosulphate solution, only a negligible amount of a red substance was deposited after standing for a day.

Freund (*Ber.*, 1884, **17**, 133) obtained a compound from malonamide and mercuric oxide to which he assigned the formula CH_2:$(CONH)_2$:Hg, because dibromomalonamide also gives a similar compound, CBr_2:$(CONH)_2$:Hg (Freund, *Ber.*, 1884, **17**, 785). However for the aforesaid reasons, dichloromercurimalonamide has been assigned the formula $(ClHg)_2$:C:$(CONH_2)_2$.

It has been observed by Naik and his co-workers that in a series like—

(*i*) $CH_2(CO{\cdot}NH_2)_2$	(*iv*) $RNH{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$
(*ii*) $RNH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH_2$	(*v*) $CN{\cdot}CH_2{\cdot}CO_2Et$
(*iii*) $CH_2(CO{\cdot}NHR)_2$	(*vi*) $CH_2(CO_2Et)_2$

the reactivity of the methylene hydrogen atoms increases from (*i*) to (*vi*). If it be assumed that the chloromercuri-group which replaces a hydrogen atom of the methylene group is attached to the carbon atom with the same degree of tenacity as the corresponding hydrogen atoms, then the decomposition of the chloromercuri-derivatives

of such compounds by potassium iodide, etc., will also be in the order of this reactivity. This has actually been found to be the case, for dichloromercurimalondiheptylamide reacts with potassium iodide more slowly than does ethyl dichloromercurimalonate.

Mercury in these compounds was estimated by the Francois' method ; while chlorine was estimated by the Carius' method, but the precipitate of silver chloride was filtered and washed in the cold, on account of the solubility of silver chloride in hot water in the presence of mercuric salts.

Experimental.

Ethyl Dichloromercurimalonate.—Ethyl malonate (2 g.) and mercuric chloride (7 g.) were dissolved in dilute (30%) alcohol and glycerol (20 c.c.) added. A solution of sodium bicarbonate (2·5 g.) was slowly added to it with constant stirring. After some time small silky needles began to come down. These were filtered after two hours and repeatedly washed with dilute alcohol. The substance is insoluble in any of the ordinary solvents. It does not melt below 300°. (Found: Hg, 64·10 ; Cl, 11·44. $C_7H_{10}O_4Cl_2Hg_2$ requires Hg, 63·59 ; Cl, 11·28 per cent.).

Action of Hydrochloric Acid on the above.—The substance (1 g.) was suspended in dilute alcohol and concentrated hydrochloric acid (10 c. c.) added. After refluxing for half an hour, the residue was filtered and washed. The filtrate was found to contain mercuric chloride. The substance was insoluble in any solvent and does not melt but turns grey at 192-5°. (Found: Hg, 50·93 ; Cl, 8·52. $C_7H_{11}O_4ClHg$ requires Hg, 50·69 ; Cl, 8·92 per cent.)

Action of Hydrogen Sulphide.—When hydrogen sulphide was slowly passed into a hot alcoholic suspension of the substance, a black precipitate of mercuric sulphide was obtained.

Action of Sodium Thiosulphate.—The substance completely went into solution in a 50 % solution of sodium thiosulphate. On standing for twenty-four hours, a very small amount of a red substance was deposited.

Action of Potassium Iodide.—(a) *Alcoholic.* The compound (0·2036 g.) was suspended in alcohol and potassium iodide (2 g.) added. After half an hour, the alkali liberated, required 3·4 c.c. of 0·098*N*-hydrochloric acid. It was then refluxed for four hours on a

water-bath, when a further amount of alkali equivalent to 3·2 c.c. of 0·098*N* hydrochloric acid was liberated.

		Calc.	Found.
Equivalent of alkali.	...	1	1·03
		2	1·99

(b) *Aqueous.* The substance was shaken for half an hour with an aqueous solution of potassium iodide, and the residue was filtered and washed with alcohol. On analysis it was found to be identical with ethyl monochloromercurimalonate. (Found : Hg, 51·15 ; Cl, 9·23 per cent).

Dichloromercurimalonamide.—Malonamide (2 g.) and mercuric chloride (11 g.) were dissolved in water, and glycerol (20 c.c.) was added. An aqueous solution of sodium bicarbonate (4 g.) was then added to it. After an hour the whole liquid became slightly yellowish. The yellow floating particles coagulated and were easily filtered. The filtrate that came down was a milky solution containing the product in colloidal suspension. It was, therefore, allowed to stand for five days, when the colloidal mass came down in small cubic crystals. This was filtered and repeatedly washed with water.

It is soluble in alcohol, benzene and ether; the pure substance shrinks at 191-2° and melts with decomposition at 220°. (Found: Hg, 70·5 ; Cl, 12·32. $C_3H_4O_2N_2Cl_2Hg_2$ requires Hg, 70·05 ; Cl, 12·43 per cent.)

Action of Bromine on the above.—Aqueous bromine was slowly added to a suspension of the compound in water, till it was no longer absorbed. The residue was filtered and recrystallised from alcohol ; m.p. 203°. It is identical with dibromomalonamide.

Dichloromercurimalondimethylamide.—It was prepared by a similar process. It is soluble in chloroform, benzene, methyl alcohol and ethyl alcohol, and melts at 241° (decomp). (Found: Hg, 66·6; Cl, 11·90. $C_5H_8O_2N_2Cl_2Hg_2$ requires Hg, 66·77; Cl, 11·85 per cent.).

Dichloromercurimalondiethylamide.—This was prepared by the same method, but in dilute alcoholic solution. It crystallised after three days in cubic crystals. It is soluble in ether, benzene, chloroform and alcohol and has no definite melting point but decomposes turning yellow at 191°. (Found: Hg, 63·5 ; Cl, 11·65. $C_7H_{12}O_2N_2Cl_2Hg_2$ requires Hg, 63·79; Cl, 11·32 per cent.)

Dichloromercurimalondipropylamide.—This was similarly prepared. The product was separated on the next day. It does not crystallise like the foregoing members if allowed to remain longer in contact with the solution, but instead gelatinises, which can neither be filtered nor separated. It is soluble in alcohol, ether, chloroform and benzene ; it changes colour at 162° and melts at 173-5°. (Found: Hg,61·5; Cl,10·72. $C_9H_{16}O_2N_2Cl_2Hg_2$ requires Hg, 61·06; Cl,10·84 per cent.).

Dichloromercurimalondibutylamide.—Prepared in the same way as above, it was washed with dilute alcohol, as it has a tendency to gelatinise in presence of ordinary sovents. This property is also shared by the following products. It is soluble in alcohol, ether, and benzene; m.p. 90°. (Found: Hg,58·4; Cl,9·95. $C_{11}H_{20}O_2N_2Cl_2Hg_2$ requires Hg, 58·56; Cl, 10·39 per cent.)

Dichloromercurimalondiisobutylamide.—It was separated on the next day. It is soluble in alcohol, ether, benzene and chloroform ; m.p. 108-9°. (Found: Hg, 58·8; Cl, 10·52. $C_{11}H_{20}O_2N_2Cl_2Hg_2$ requires Hg, 58·56; Cl,10·39 per cent.)

Preparation of Malondiamylamide.—This was prepared by the same method as used by Backes, West and Whiteley (*J. Chem. Soc.*, 1921, **119**, 359) for the preparation of alkylmalonamides. Ethyl malonate (8 g.) and amylamine (8·7 g.) were mixed up in a sealed tube and allowed to remain at ordinary temperature for 24 hours, and then heated at 120°, for six hours. After cooling, the solid was washed out with petroleum and recrystallised from benzene m.p. 126° (yield, 80 %) It is very soluble in benzene, alcohol, ether, chloroform and carbon tetrachloride but slightly so in petroleum. (Found: N, 12·0. $C_{13}H_{26}O_2N_2$ requires N, 11·57 per cent.)

Dichloromercurimalondiamylamide.—The product became quite granular within three hours and could therefore be separated. It was converted into a gelatinous product even on standing for a day. It melts with decomposition at 143°. (Found: Hg, 56·5; Cl,9·94. $C_{13}H_{24}O_2N_2Cl_2Hg_2$ requires Hg, 56·25; Cl, 9·98 per cent.)

Malondiisoamylamide.—Amylamine (9 g.) and ethyl malonate (8 g.) were mixed up in a sealed tube and allowed to remain for a day. This was, afterwards, heated for 12 hours at 200°. The contents were taken out and concentrated on a water-bath, when a thick syrupy liquid was obtained. This was allowed to remain at ordinary temperature for three days, when long needles separated.

These were separated by washing with the least amount of petroleum and recrystallised from benzene (yield, 20%).

It is very soluble in alcohol, benzene, chloroform, ether and acetic acid but less so in petroleum and water; m.p. 55°. (Found : N, 12·1. $C_{13}H_{26}O_2N_2$ requires N, 11·57 per cent.)

Dichloromercurimalondiisoamylamide.—It was prepared from malondiisoamylamide. It is soluble in alcohol, benzene, chloroform and ether; m.p. 105°. (Found: Hg, 56·3; Cl, 9·85. $C_{13}H_{24}O_2N_2Cl_2Hg_2$ requires Hg, 56·25; Cl, 9·98 per cent.)

Dichloromercurimalondiheptylamide.—This was prepared like the other compounds and separated after two hours; m.p. 117°. (Found : Hg, 52·4 ; Cl, 9·50. $C_{17}H_{32}O_2N_2Cl_2Hg_2$ requires Hg, 52·15 ; Cl, 9·25 per cent.)

Action of Alcoholic Potassium Iodide on the Above.—The dry substance (0·1890 g.) was suspended in alcohol and an alcoholic solution of potassium iodide (2 g.) was added. Even after two days an amount of alkali equivalent to 1·5 c.c. of 0·098*N*-hydrochloric acid was liberated. It was then refluxed for six hours, when the total amount of alkali liberated was found to be equivalent to 5 c.c. of 0·098*N*-hydrochloric acid.

	Calc.	Found.
Equivalent of alkali ...	2	1·97

Action of Hydrochloric Acid.—The substance (0·5 g.) was suspended in water and 1 c.c. of concentrated hydrochloric acid was added. On heating for fifteen minutes a white substance was obtained which was crystallised from alcohol and found to be identical with malondiheptylamide.

The authors take this opportunity to record their gratitude to the Government of His Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work. One of the authors (C. C. S.) desires to express his gratitude to His Highness the Maharaja of Rajpipla for a scholarship, which enabled him to carry out this research.

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Aromatic Disulphides and Sugden's Parachors. Part IV.

By S. S. Bhatnagar and Balwant Singh.

Sulphur exhibits covalencies of one, two, three, four and six in combination with other elements. With another sulphur atom it forms a strong link and in consequence, long chains of sulphur atoms are readily formed. Lecher (*Ber.*, 1915, **48**, 524 and subsequent papers) has shown that diphenyldisulphide, di-*p*-dimethylaminodiphenyldisulphide, di-*o*-nitrophenyldisulphide and *o*-nitrodiphenyldisulphide exhibit thermochromic properties. This change in colour might be due to dissociation into free radicles, as, such dissociation has been observed in the case of nitrogen (in tetra-aryl hydrazines, Wieland, *Annalen*, 1912, **392**, 156) and oxygen (in some aromatic peroxides, Pummerer and Cherbuliez, *Ber.*, 1914, **47**, 2957).

Lecher (*Ber.*, 1925, **58**, 417) attempted to apply to compounds of sulphur those methods (such as replacement of the group R in the compound RX·XR by the group RX), which have been shown to promote dissociation into radicles in the cases of compounds of nitrogen and carbon, but he failed to get any evidence of the existence of radicles with univalent sulphur. He, therefore, concluded that the colour changes are due not to dissociation into free radicles or to rearrangement of the atoms, but to a redistribution of the valencies.

In this investigation some of the aromatic disulphides have been studied in the fused state by the method of parachor determination. The parachor method has been extensively employed by Sugden (*J. Chem. Soc.*, 1925, **127**, 1525 and subsequent papers) ; see also Bhatnagar and others (*J. Chim. phys.*, 1928, **25**, 21; *J. Indian Chem. Soc.*, 1929, **6**, 263).

Experimental.

I. 1. Diphenyldisulphide, m.p. 66·5°.
2. 4:4′-Dichlorodiphenyldisulphide, m.p. 71·5°.
3. 4:4′-Dibromodiphenyldisulphide, m.p. 93·8°.

4. 4:4′-Dimethyldiphenyldisulphide, m.p. 46·0°.

5. 4:4′-Dimethoxydi-*m*-tolyldisulphide, m.p. 73·5°.

6. *ββ′*-Dinaphthyldisulphide, m.p. 139·0° (prepared by the method of Stewart, *J. Chem. Soc.*, 1922, **121**, 2555).

II. 1. Dibenzyldisulphide, m.p. 71·0°.

2. 2:2′-Dinitrodibenzyldisulphide, m.p. 112·0° (obtained by the method of Price and Twiss, *J. Chem. Soc.*, 1909, **95**, 1490).

Density was determined with a U-shaped pyknometer (Sugden, *J. Chem. Soc.*, 1924, **125**, 1171) and surface tension by the method of maximum bubble pressure with an apparatus previously described by the authors (*loc. cit.*). The results are given in Table I.

TABLE I.

Substance.	Temperature.	Density. g./c.c.	Surface tension dynes/cm.	Parachor, Pobs.
1. Diphenyldisulphide ..	64·9°	1·155	40·58	476·8
	79·1°	1·142	39·03	477·6
	96·8°	1·127	37·29	478·5
	118·0°	1·110	35·08	478·5
			Mean	477·9
2. 4:4′-Dichlorodiphenyldisulphide.	76·2°	1·328	41·90	550·1
	88·1°	1·317	40·55	550·1
	102·3°	1·304	39·38	550·7
			Mean	550·6
3. 4:4′-Dibromodiphenyldisulphide.	99·0°	1·664	41·90	575·0
	115·0°	1·647	40·33	575·3
	136·0°	1·626	38·51	576·1
	152·0°	1·610	37·24	577·1
			Mean	575·9
4. 4:4′-Dimethyldiphenyldisulphide.	51·2°	1·114	39·00	552·5
	69·3°	1·100	37·30	553·1
	89·2°	1·084	35·00	552·5
	111·0°	1·068	33·13	553·3
			Mean	559·2

	Substance.	Temperature.	Density. g./c.c.	Surface tension dynes/cm.	Parachor, Pobs.
5.	4 :4′-Dimethoxydi-*m*-tolyldisulphide.	76·8°	1·160	40·15	664·5
		89·7°	1·149	38·86	665·5
		100·5°	1·139	37·84	666·8
		117·0°	1·126	36·23	667·4
				Mean	666·1
6.	ββ′-Dinaphthyldisulphide.	144·0°	1·144	37·20	687·1
		155·0°	1·138	36·98	689·5
		169·0°	1·128	36·24	692·1
				Mean	689·6
7.	Dibenzyldisulphide.	75·2°	1·105	38·73	555·9
		88·0°	1·094	37·43	556·7
		100·2°	1·085	36·42	557·5
		112·5°	1·075	35·26	558·1
				Mean	557·1
8.	2 :2′-Dinitrodibenzyldisulphide.	115·0°	1·308	44·81	665·3
		125·0°	1·298	43·53	665·3
		140·0°	1·286	42·25	666·5
				Mean	665·7

Discussion.

If an element possesses n valency electrons, then its normal valency is n or $8-n$, whichever is the smaller. Higher valencies may be ascribed to—(1) the transference of electrons from one atom to another as in polar bonds and in semi-polar double bonds, (2) the sharing of more than the normal number of electrons and (3) the formation of singlet linkages.

An atom of sulphur possesses six valency electrons and on the above hypothesis its nornal valency is two. In aromatic disulphides the sulphur atom may be divalent and might exert a higher valency of four or six, by sharing more than the normal number of electrons

with the second sulphur atom in the molecule. An aromatic disulphide, thus, may have any of the structures given below:—

$$\underset{\text{(I)}}{Ar{\cdot}S{\cdot}S{\cdot}Ar} \qquad \underset{\text{(II)}}{Ar{\cdot}S{\cdot}Ar \;\|\; S} \qquad \underset{\text{(III)}}{Ar{\cdot}S{\equiv}S{\cdot}Ar} \qquad \underset{\text{(IV)}}{Ar{\cdot}S{\equiv\!\!\equiv}S{\cdot}Ar.}$$

In every case the shell of eight electrons around each sulphur atom is not exceeded.

Assuming the above structures for the disulphides, their parachors are calculated from the constants of Sugden (*J. Chem. Soc.*, 1924, **125**, 1180 and subsequent papers). The parachor for naphthalene ring has been taken from a previous paper of the authors (*loc. cit.*). The parachors $P_{calc.}$ so obtained in each case are compared with the parachors $P_{obs.}$ obtained from the surface tension data in Table II.

TABLE II.

	Substance.	$P_{obs.}$	P			
			Structure I.	Structure II.	Structure III.	Structure IV.
1.	Diphenyldisulphide ...	477·9	476·4	499·6	522·8	569·2
2.	4 :4′-Dichlorodiphenyldisulphide ...	550·6	550·8	574·0	597·2	643·6
3.	4 :4-′Dibromodiphenyldisulphide ...	575·9	578·2	601·4	624·6	671·0
4.	4 :4′-Dimethyldiphenyldisulphide ...	552·9	554·4	577·6	600·8	647·2
5.	4 :4′-Dimethoxydi-*m*-tolyldisulphide ...	666·1	672·4	695·6	718·8	765·2
6.	ββ′-Dinaphthyldisulphide ...	689·6	688·2	711·4	734·6	781·0
7.	Dibenzyldisulphide ...	557·1	554·4	577·6	600·8	647·2
8.	2 :2′-Dinitrodibenzyldisulphide ...	665·7	668·6	691·8	715·0	761·4

From the above table it is evident that the parachors $P_{calc.}$ calculated according to the structure (I) are in good agreement with the observed parachors, except in case of 4 :4′-dimethoxydi-*m*-tolyldisulphide where the values differ by 6·3 units. This appears to be due to association. The associated liquids, *viz.*, alcohols, phenols and fatty acids, etc., give parachors 4-8 units lower than the calculated

(Sugden, *J. Chem. Soc.*, 1924, **125**, 1185; Jones, *J. Chem. Soc.*, 1928, p. 1196; and Hunten and Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 161). Since 4:4′-dimethoxydi-*m*-tolyldisulphide contains two substituted hydroxy groups, namely, two methoxy groups, it should behave similarly in the fused state and the low value of its parachor is thus accounted for.

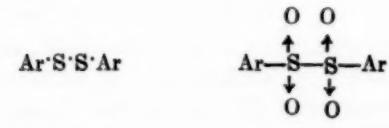
These large parachor differences in the other cases cannot be explained on any abnormal behaviour, which the aromatic disulphides might exhibit in the fused state. Sulphur is neither quadrivalent nor hexavalent but is found to be bivalent in the disulphides in the fused state.

An aromatic disulphide is thus represented by the structure (I).

Chemical formula. (I) Electronic formula.

Each sulphur atom in the molecule forms two normal covalencies to complete its octet. Of these eight electrons, one pair is shared with a carbon atom of the aromatic group and another pair is shared with the second sulphur in the molecule; while the other four are not shared and form two "lone" pairs around each sulphur atom.

Although each sulphur atom in the molecule is in this sense saturated, it can form two more co-ordinate covalencies by sharing these "lone" pairs with atoms, for example of oxygen, which need two electrons to complete their octet. Thus the possibility of co-ordination enables the sulphur atom to increase its covalency from two to four, which explains the formation of an aromatic disulphone from an aromatic disulphide.



Disulphide. Disulphone.

Summary.

1. Surface tension and density of diphenyldisulphide, 4:4′-dichlorodiphenyldisulphide, 4:4′-dibromodiphenyldisulphide, 4:4′-dimethyldiphenyldisulphide, 4:4′-dimethoxydi-*m*-tolyldisulphide, ββ′-dinaphthyldisulphide, dibenzyldisulphide, 2:2′-dinitrodibenzyldisulphide have been determined at various temperatures in the fused state.

2. Parachors for these substances in the fused state have been calculated from the observed data as well as from the values of atomic and structural constants.

3. Sulphur exerts its normal valency (*viz.*, two) in these aromatic disulphides in the fused state.

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Condensation of Ethyl Acetoacetate with Aromatic Amines. Part I.

By G. V. Jadhav.

Ethyl acetoacetate gives different condensation products with aromatic amines, according to the conditions of reaction. Knorr (*Ber.*, 1883, **16**, 2593) at first regarded the product obtained from aniline and acetoacetic ester to be $Me{\cdot}C(NHPh){=}CH{\cdot}CO_2Et$, but later on (*Ber.*, 1884, **17**, 542) he changed his views and assigned the constitution, $Me{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHPh$. He worked with aniline, *o*-, *m*- and *p*-toluidines, naphthylamines and *o*-phenylenediamine.

Later on Conard and Limpach (*Ber.*, 1888, **21**, 521) carried out the condensation of the same and some other amines at room temperature with the methyl ester and found that the products obtained were the derivatives of crotonic acid, namely $Me{\cdot}C(NHR){=}CH{\cdot}CO_2Me$. The same workers also condensed the ethyl ester with *p*-anisidine and got a similar product (*Ber.*, 1888, **21**, 1651). Later on Ewing and King extended the work of Knorr to prepare new dimethyltetrahydroquinolines (*J. Chem. Soc.*, 1913, **113**, 106).

No attempt seems to have been made to see the effect of substituents in the nucleus on the course of the reaction. The present work was undertaken to prepare some substituted quinoline derivatives, which would be described later on.

o-, *m*-, and *p*-Nitroanilines, *o*-, *m*-, and *p*-chloroanilines, *p*-anisidine, *p*-phenetidine and *m*-xylidines (1:4:5 and 1:3:4) were empolyed. Of these *o*-nitroaniline did not condense even after prolonged boiling with ethyl acetoacetate. The condensation products of the other amines could be divided into three classes:

(*i*) $Me{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHR$

(*ii*) $Me{\cdot}C(NHR){:}\,CH{\cdot}CO_2Et$

and (*iii*) $Me{\cdot}C(NHR){:}\,CH{\cdot}CO{\cdot}NHR$.

The substances of the type (*iii*) are decomposed by hydrochloric acid giving substances of the type (*i*), in the case of *m*- and *p*-

nitroanilines, while the compounds obtained from other amines are perfectly stable even towards boiling hydrochloric acid.

The compounds of the type (*ii*) are obtained in the case of *p*-nitroaniline, *p*-chloroaniline and *p*-phenetidine. In the last two cases the reaction takes place at room temperature. Anilides of type (*i*) are obtained in the case of *m*-nitroaniline, *o*-,*m*- and *p*-chloroanilines and *p*-anisidine. Xylidines give products of the type (*iii*). It should be noted however that products of the type (*iii*) together with varying proportions of other products either of the type (*i*) or (*iii*) are obtained in all cases, if the reaction mixture is heated for a longer time. The substances of the type (*i*) and (*ii*) do not give any colouration with ferric chloride, but those of the type (*i*) give violet to blue colour as expected.

The latter react with ammonia giving aminocrotonanilides as obtained by Knorr (*Ber.*, 1892, **25**, 775). In the case of *p*-anisidine, *p*-phenetidine and the chloroanilines, water separates out from the reaction mixture as soon as they are mixed with ethyl acetoacetate but the isolation of the pruduct at this stage is found possible only in two cases, *viz.*, *p*-phenetidine and *p*-chloroaniline. If the same mixture is heated, the product is an anilide (type *i*). It therefore seems that an ester of the aminocrotonic acid is first formed and the water liberated in the reaction then hydrolyses the aminoester and the more stable amide is formed.

The formation of compounds of the type (*iii*) together with those of type (*i*) and (*ii*) can be explained as follows:—

A little of the latter that are formed reacts with free amines forming some of the type (*iii*). Thus there is always an equilibrium between the two.

That the reaction takes the above course in the formation of compounds of type (*iii*) is supported by the fact that the anilide (type *i*) or anilinocrotonic ester (type *ii*) when heated with an aniline gives a compound of the type (*iii*).

The stability of the compounds depends upon the basicity of the anilines used as is suggested by Fierz-David and Ziegler (*Helv. Chim. Acta*, 1928, **11**, 776). This is also proved by the fact that the diamides (type *iii*) of nitroanilines (which are less basic) are hydrolysed by hydrochloric acid in the cold into anilines and mono-anilides (*i*). While similar compounds of chloroanilines, methoxy-, and ethoxy-anilines and xylidines are perfectly stable towards the same acid even when boiled with it.

Experimental.

Acetoacet-m-*nitroanilide*.—Ethyl acetoacetate (10 g.) was mixed with *m*-nitroaniline (10 g.) when heat was absorbed. The mixture was then refluxed with an air condenser for about four hours. The red liquid was then allowed to cool. On cooling some solid was obtained. It was then heated on a water-bath for about three hours to remove the alcohol formed in the reaction. The solid obtained was then triturated with ether to remove the adhering ester and unacted amine and washed with it. The residue crystallised as pale yellow needles from boiling water, m. p. 120-21°. It is soluble in most organic solvents like alcohol, chloroform, acetic acid and difficultly soluble in ether and benzene. (Found: N, 12·80. $C_{10}H_{10}O_4N_2$ requires N, 12·61 per cent.). A deep yellow solid insoluble in water was also obtained.

β-m-*Nitroanilinocroton*-m-*nitroanilide*.—The ester (10 g.) and the amine (15 g.) were mixed and heated as before for about ten hours. After the removal of alcohol, the product was washed as before with ether. The mono-amide formed is removed by repeated boiling with water. The yellow insoluble portion is then crystallised from a large quantity of benzene, m. p. 152-153°. The same compound is obtained if the monoanilide obtained in the previous experiment is heated at 140-150° for about four hours with *m*-nitroaniline. (Found: N, 16·40. $C_{16}H_{14}O_5N_4$ requires N, 16·38 per cent.).

Action of Hydrochloric Acid on β-m-*Nitroanilinocroton*-m-*nitroanilide*.—The substance (1 g.) was treated with cold hydrochloric acid (3 c.c.). The yellow solid began to change colour and became white. After about one hour, it was filtered and washed with water till free from acid. The insoluble substance was then crystallised from boiling water in pale yellow needles, m. p. 119-120°. Mixed melting point with acetocet-*m*-nitroanilide described before is also 119-120°.

Action of Ammonia on Acetoacet-m-*nitroanilide*: *Formation of β-Amidocroton*-m-*nitroanilide*.—The anilide (1 g.) and concentrated ammonia in excess were boiled for 15-20 minutes, more ammonia being added at intervals. The orange coloured turbid solution gave orange-red needles on cooling. These were washed with cold water till free from ammonia, and were found to be soluble in alcohol and benzene, m. p. 129-130°. (Found: N, 18·74. $C_{10}H_{11}O_3N_3$ requires N, 19·00 per cent.).

Ethyl β-p-Nitroanilinocrotonate.—Ethyl acetoacetate (10 g.) and *p*-nitroaniline (10 g.) were mixed and boiled under a reflux condenser for about five hours. The alcohol was removed from the mixture by heating on a water-bath for about an hour. On cooling an orange solid was obtained. It was then triturated and washed with benzene when the orange coloured solid remained behind and the benzene solution on evaporation gave a yellow solid. The latter crystallised from alcohol in needles, m. p. 122-123°. (Found: N, 11·46. $C_{12}H_{14}N_2O_4$ requires N, 11·20 per cent.).

β-p-Nitroanilinocroton-p-nitraonilide.—The orange coloured solid insoluble in benzene in the previous experiment was extracted with boiling water to remove the unacted *p*-nitroaniline. The orange solid insoluble in water was found to be insoluble in most organic solvents. It was crystallised from boiling nitrobenzene in orange needles, m. p. above 250°.

If the compound of m. p. 122-128° obtained in the previous experiment is heated with *p*-nitroaniline at 160-170° for five hours it gives the same compound. (Found: N, 16·03. $C_{16}H_{14}O_5N_4$ requires N, 16·38 per cent.).

Action of Hydrochloric Acid on β-p-Nitroanilinocroton-p-nitroanilide: Formation of Acetoacet-p-nitroanilide—The compound (1 g.) was treated with cold hydrochloric acid (5 g.). The orange solid began to change colour at once and became yellow. It was left in contact with the acid for about half an hour with occasional stirring. It was then filtered and washed free from acid. The insoluble mass was crystallised from alcohol in needles, m. p. 122-123°. Mixed melting point with ethyl *β-p*-nitroanilinocrotonate was 100-105°. This anilide when heated with *p*-nitroaniline at 140-150° gives the dianilide described before. This seems to be identical with that described by Fierz-David and Ziegler (*loc. cit.*) who gives its m. p. 119°. (Found: N,12·89. $C_{10}H_{10}O_4N_2$ requires N, 12·61 per cent.).

β-Aminocroton-p-nitroanilide.—The anilide (1 g.) was heated with strong ammonia for about 15 minutes with occasional addition of fresh ammonia. On cooling, yellow needles were obtained. These were collected and washed free from ammonia, m. p. 189-190°. (Found: N, 18·73. $C_{10}H_{11}O_3N_3$ requires N, 19·0 per cent.).

Acetoacet-p-anisidide.—*p*-Anisidine (10 g.) and ethyl acetoacetate (10 g.) were heated under a reflux condenser in an oil-bath at 130-140° for about eight hours. The dark greenish mixture was allowed to cool when a solid separated out, which was washed with

ether to remove some adhering oil. It was soluble in most organic solvents, and crystallised from boiling water in irregular plates, m. p. 117-118°. (Found: N, 7·03. $C_{11}H_{13}O_3N$ requires N, 6·76 per cent.).

β-Aminocroton-p-*anisidide*.—The anisidide (1 g.) was mixed with strong ammonia when it went into solution which was shaken for three hours and then left overnight. Next day when ammonia was evaporated off at room temperature, a solid separated. This was then filtered, washed free from ammonia and crystallised from ether in needles, m. p. 109-110°. (Found: N, 13·34. $C_{11}H_{14}O_2N_2$ requires N, 13·58 per cent.).

β-p-*Anisidino*-p-*anisidide* —Ethyl acetoacetate (10 g.) and *p*-anisidine (10 g.) were boiled under reflux for about an hour; when the red liquid was allowed to cool, it gave some solid. It was then diluted with alcohol and washed with it. The solid was then crystallised from glacial acetic acid in needles, m. p. 235-236°. This same compound is obtained by heating acetoacet-*p*-anisidide with *p*-anisidine at 160-170° for about 5 hours. (Found: N, 9·21. $C_{18}H_{20}O_3N_2$ requires N, 8·97 per cent.).

Ethyl p-*Phenetidinocrotonate*.—Ethyl acetoacetate (10 g.) and *p*-phenetidine (10 g.) were mixed. When the mixture began to get turbid due to the separation of water, it was put in a desiccator. After two days, a crystalline solid separated out. As it was found to be easily soluble in common organic solvents, the solid was allowed to dry on a porous plate for some days. It crystallised from dilute alcohol in irregular plates m. p. 60-61°. (Found: N, 6·04, $C_{14}H_{19}O_3N$ requires N, 5·62 per cent.).

β-p-*Phenetidinocroton*-p-*phenetidide*.—Ethyl acetoacetate (10 g.) and *p*-phenetidine (10 g.) were boiled under a reflux condenser for about 45 minutes. When signs of solid formation were visible, the hot mixture was allowed to cool. It was then triturated and washed with ether to remove the adhering oil. The solid was crystallised from glacial acetic acid, m.p. 230-231°.

This substance was also obtained by heating ethyl *β-p*-phenetidinocrotonate with *p*-phenetidine at 160-170° for 5 hours. (Found: N, 8·41. $C_{20}H_{24}O_3N_2$ requires N, 8·24 per cent.).

β-m-(1 : 4 : 5)-*Xylidinocroton*-m-(1 : 4 : 5)-*xylidide*.—Xylidine (12 g.) and the ester (13 g.) were mixed together and rapidly boiled under reflux for about one hour. On cooling a solid separated out which

was triturated with alcohol to remove the adhering oily impurities. It was practically insoluble in alcohol, benzene, toluene, ether, chloroform or acetone. It crystallised from glacial acetic acid, m. p. above 275°. (Found: N, 9·33. $C_{20}H_{24}ON_2$ requires N, 9·09 per cent.).

β-m-(1 : 3 : 4)-*Xylidinocroton*-m-(1 : 3 : 4)-*xylidide*.—The reaction was carried out as in the preceding case, the heating being continued for about two hours. It is insoluble in most organic solvents. It crystallised from glacial acetic acid in needles, m. p. above 275°. (Found: N, 9·16. $C_{20}H_{24}ON_2$ requires N, 9·09 per cent.).

Acetoacet-m-*chloroanilide*.—Ethyl acetoacetate (10 g.) and *m*-chloroaniline (10 g.) were boiled under reflux for about one hour. The brown liquid was heated on a water-bath to remove alcohol. On cooling the liquid gave a crystalline solid. It was then triturated and washed with ether to remove the excess of the ester and the amine. The solid was found easily soluble in most common organic solvents but difficultly in boiling water. It crystallised from dilute acetic acid in irregular plates, m. p. 105-106°. (Found: Cl, 16·68; N, 6·97. $C_{10}H_{10}O_2NCl$ requires Cl, 16·78 ; 6·62 N, per cent.).

β-m-*Chloroanilinocroton*-m-*chloroanilide*.—Ethyl acetoacetate (5 g.) and *m*-choloroaniline (7 g.) were boiled with an air condenser for two hours and the red liquid was then allowed to cool. The pasty mass was washed with ether and the solid crystallised from alcohol in needles, m.p. 240-241°. The same substance was obtained by heating acetoacet-*m*-chloroanilide with *m*-chloroaniline at 160-170° for about 4 hours. (Found: Cl, 22·30; N, 8·59. $C_{16}H_{14}ON_2Cl_2$ requires Cl, 22·12 ; N, 8·72 per cent.).

Acetoacet-p-*chloroanilide*.—The ester (10 g.) and the amine (10 g.) were mixed and boiled with a reflux condenser for about two hours. The mixture was then allowed to cool when a solid separated out. It was then washed with ether to remove the unacted ester and amine, when a white crystalline substance was obtained, which crystallised from boiling water, m.p. 132-133°. (Found: Cl, 16·67; N, 7·08. $C_{10}H_{10}O_2NCl$ requires Cl, 16·78; N, 6·62 per cent.).

β-Aminocroton-p-*chloroanilide*.—Acetoacet-*p*-chloroanilide (1 g.) was mixed with liquor ammonia, when the solid went into solution; the solution was shaken for about six hours. Much solid separated out from the solution which was filtered off and washed free from ammonia. The mother-liquor gave more solid as ammonia evaporated, m. p.

110°. (Found: N, 12·95; Cl, 16·72. $C_{10}H_{11}ON_2Cl$ requires N, 13·30; Cl, 16·87 per cent.).

Ethyl β-p-Chloroanilinocrotonate.—Ethyl acetoacetate (15 g.) and *p*-chloroaniline (15 g.) were mixed in a beaker. When the solution began to be turbid due to the separation of water, it was kept in a desiccator. After three days a crystalline solid separated out. As it was very soluble in most organic solvents, it was dried on a porous plate. The solid was finally crystallised from alcohol in needles, m.p. 55°. (Found: Cl, 14·48; N, 6·07. $C_{12}H_{14}O_2NCl$ requires Cl, 14·82; N, 5·85 per cent.).

β-p-Chloroanilinocroton-p-chloroanilide.—Ethyl acetoacetate (5 g.) and *p*-chloroaniline (10 g.) were boiled with a reflux condenser for about two hours. A solid separated, when the heating was stopped. It was washed with benzene, when colourless needles were obtained, m.p. above 275°. The same substance was obtained by heating acetoacet-*p*-chloroanilide or ethyl *β-p*-chloroanilinocrotonate with *p*-chloroaniline at 140-150° for five hours. (Found: Cl, 22·48; N, 8·82. $C_{16}H_{14}ON_2Cl_2$ requires Cl, 22·12: N, 8·72 per cent.).

Acetoacet-o-chloroanilide.—The ester (10 g.) and *o*-chloroaniline (10 g.) were mixed and refluxed with an air condenser for about twenty minutes. The yellowish liquid was then heated on a water-bath to remove the alcohol formed in the reaction. On allowing the reddish liquid to cool, crystals were obtained which when filtered and washed with ether became white. These crystallised from very dilute alcohol in needles, m.p. 107-108°. This is the same as described by Fierz-David and Ziegler (*loc. cit.*). It is easily soluble in alcohol, chloroform, benzene, acetone and glacial acetic acid. (Found: Cl, 16·46; N, 6·91. $C_{10}H_{10}O_2NCl$ requires N, 6·62; Cl, 16·78 per cent.).

A small solid residue insoluble in alcoholic water was left behind which was crystallised from alcohol; m.p. 236°.

β-Aminocroton-o-chloroanilide.—Some of the anilide obtained in the previous experiment was mixed with liquor ammonia, when the solid went into solution. The solution was shaken for six hours and left overnight. It was again shaken next day for six hours more. Some solid separated out which was filtered and washed free from ammonia. The solution left on evaporation of the ammonia at room temperature gave more solid, m. p. 96-97°. (Found: N, 13·54; Cl, 16·98. $C_{10}H_{11}ON_2Cl$ requires N, 13·30; Cl, 16·87 per cent.).

β-o-*Chloroanilinocroton*-o-*chloroanilide*.—The ester (10 g.) and aniline (15 g.) were mixed and refluxed with an air condenser for about an hour and a half. The red liquid was allowed to cool when a solid separated out. The mixture was triturated and washed with ether to remove the adhering oily impurity. The white solid thus obtained was insoluble in water and was crystallised from boiling alcohol. By mixed m.p. it was identified with the solid obtained in the previous experiment in a very small quantity. Its m. p. was 236°. The same compound is obtained by heating acetoacet-*o*-chloroanilide with *o*-chloroaniline at 140-150° for about five hours. (Found: Cl, 21·85; N, 9·12. $C_{16}H_{14}ON_2Cl_2$ requires Cl, 22·12; N, 8·72 per cent.).

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Chemical Reactions in Infra-red Radiations. Part II.

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In a recent communication (Bhattacharya and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 451) we have shown that several chemical changes can be accelerated by radiations of mean wave-length 7304Å. In this paper we are recording our results on the acceleration of some other reactions by radiations of the same mean wave-length and wave-lengths longer than 7304Å.

Some years ago Wood ("Physical Optics," 1911, p. 15) stated that a light filter consisting of a saturated solution of potassium dichromate placed in a cobalt-glass cell of one centimetre thickness cuts off all radiations shorter than 6900Å. Ellis and Wells ("Chemical Action of Ultra-violet Rays," 1925, p. 80) state that the same filter only transmits infra-red rays of wave-lengths longer than 10140Å.

By using a copper arc and a photographic plate sensitised by neocyanin, we have observed that the above filter cuts off all radiations

shorter than 8000Å. It will be seen in the above photograph that the copper line 8000Å is partially transmitted by a saturated

solution of potassium dichromate placed in a cobalt-glass cell of one centimetre thickness. Anti-screen photographic plates were sensitised by dipping in a bath containing the following substances:—

Water alcohol mixture (85 :60) = 150 c.c. + neocyanin solution (1 : 2000 in C_2H_5OH) = 1·5 c.c. + kryptocyanin solution (1 : 1000 in C_2H_5OH) = 2 c.c. + dicyanin solution (1 : 100 in C_2H_5OH) 2·5 c.c. + conc. NH_4OH = 5·5 c.c.

The plate was soaked for 5 minutes in the above bath and rinsed for $\frac{1}{2}$ minute in alcohol and was rapidly dried.

Moreover by using a Nutting's spectrophotometer, we have been able to make sure that the same filter can completely cut off all visible radiations.

We have measured the velocity of sixteen chemical reactions in radiations from a 1000-watt gas-filled tungsten filament lamp filtered by the dichromate and cobalt glass filter. It appears that the mean wave-length of radiation transmitted by this filter is 8500 Å.

The experimental arrangement was the same as described in the previous paper (*J. Indian Chem. Soc.*, 1929, **6**, 451).

The experimental results are recorded in the following tables.

TABLE I.

Hydrazine Hydrochloride and Iodine at 25°.

$$N_2H_4 + 2I_2 = N_2 + 4HI.$$

N/5-Hydrazine hydrochloride = 5 c.c. *N*/100-Iodine = 10 c.c.

1·25*N*-Hydrochloric acid = 5 c.c.

Region $\lambda = 8500$ Å.

Time in minutes ...	0	20	40	60	70
Thiosulphate per 3 c.c. of the reacting mixture ...	6·8	5·35	4·2	3·3	2·9 c.c.
k_1 (Unimolecular) ...	—	0·00522	0·00523	0·00523	

Mean 0·00523

Temperature.	Vel. of reaction in the dark. k_1	Vel. of reaction in $\lambda = 7304$ Å k_1	Vel. of reaction in $\lambda = 8500$ Å. k_1	Temperature coefficient (dark).	Temp. coeff. after deducting the dark reaction. $\lambda = 7304$ Å.	Temp. coeff. after deducting the dark reaction. $\lambda = 8500$ Å.	Quantum yield. $\lambda = 7304$ Å.	Quantum yield. $\lambda = 8500$ Å.
25°	0·00465	0·00589	0·00523				4	2
35°	0·0121	0·0148	0·0134	2·60	2·18	2·24	7·4	3·8
45°	0·0302	0·0358	0·0330	2·50	2·03	2·15	9·6	4·9

Calculation of Quantum Yield.

The dimension of the observation cell is $(3 \text{ cm.})^3$ internally. The energy per quantum (corresponding to $\lambda = 8500$ Å) $= 2{\cdot}3 \times 10^{-12}$ ergs.

The radiomicrometer was calibrated for the amount of energy absorbed to produce 1 mm. deflection on the scale by using a Hefner lamp under standard conditions. This value of the energy was found to be 2·85 ergs per sec. per sq. cm.

	Deflection (cm.).	Difference in deflection (cm.).
Distilled water ...	22·6	
Reacting mixture ...	20·6	2

Hence the absorption of energy by the solute $= 20 \times 2{\cdot}85$ ergs per sec. per sq. cm.

The number of quanta absorbed by the solute per sec. per sq. cm.

$$\frac{20 \times 2{\cdot}85 \times 10^{12}}{2{\cdot}3} = 2{\cdot}48 \times 10^{13}.$$

In 70 minutes the change in the amount of iodine in light corresponds to a decrease of 3·9 c.c. of $N/452$-thiosulphate solution per 3 c.c. of the reacting mixture. In the dark the corresponding change is 3·59 c.c. of the same thiosulphate solution.

Therefore in pure light the decrease $= 3{\cdot}9 - 3{\cdot}59 = 0{\cdot}31$ c.c.

Hence, the rate of transformation of iodine molecules per sec. per sq. cm.

$$= \frac{0{\cdot}31 \times 6{\cdot}06 \times 10^{23} \times 3}{70 \times 60 \times 452 \times 1000 \times 2 \times 3} = 4{\cdot}9 \times 10^{13}$$

Therefore

$$\frac{\text{No. of mols transformed}}{\text{No. of quanta absorbed}} = \frac{4{\cdot}9}{2{\cdot}48} = 2.$$

Hydroxylamine Hydrochloride and Iodine.

$$2NH_2OH + I_2 = N_2 + 2H_2O + 2HI.$$

$N/5$-Hydroxylamine hydrochloride = 5 c.c. $N/100$-Iodine = 10 c.c. $1{\cdot}25N$-Hydrochloric acid = 5 c.c.

Temperature.	Vel. of reaction in the dark. k_1	Vel. of reaction in $\lambda = 7304$ Å. k_1	Vel. of reaction in $\lambda = 8500$ Å. k_1	Temp. coeff. (dark).	Temp. coeff. after deducting the dark reaction. $\lambda = 7304$ Å.	Temp. coeff. after deducting the dark reaction. $\lambda = 8500$ Å.	Quantum yield. $\lambda = 7304$ Å.	Quantum yield. $\lambda = 8500$ Å.
20°	0·00535	0·00646	0·00592				3·5	2·35
30°	0·0136	0·0161	0·0146	2·54	2·25	2·28	5·4	3·8
40°	0·0333	0·0388	0·0362	2·45	2·20	2·23	8·2	5·6

Inversion of Cane Sugar.

20% Cane sugar = 15 c.c. $N/20$-Hydrochloric acid = 5 c.c.

The inversion was followed by using a polarimeter.

	k_1	k_1	k_1	k_{30}/k_{20}	k_{40}/k_{30}	k_{40}/k_{20}	145	112
30°	0·0000925	0·0001096	0·000101					
35°	0·000189	0·000212	0·000203	3·85	3·70	3·75	162	142
40°	0·000727	0·000812	0·000780				193	163

Oxalic Acid and Chlorine.

$N/75$-Chlorine = 10 c.c. $1{\cdot}25N$-Hydrochloric acid = 5 c.c. $N/5$-Oxalic acid = 5 c.c.

Temperature.	Vel. of reaction in the dark. k_1	Vel. of reaction in $\lambda = 7304$ Å. k_1	Vel. of reaction in $\lambda = 8500$ Å. k_1	Temp. coeff. (dark).	Temp. coeff. after deducting the dark reaction. $\lambda = 7304$ Å.	Temp. coeff. after deducting the dark reaction. $\lambda = 8500$ Å.	Quantum yield. $\lambda = 7304$ Å.	Quantum yield. $\lambda = 8500$ Å.
15°	0·0119	0·0149	0·0131				$2{\cdot}1 \times 10^2$	63
25°	0·0351	0·0426	0·0384	2·95	2·5	2·75	$4{\cdot}9 \times 10^2$	75
35°	0·102	0·120	0·111	2·90	2·42	2·72	$8{\cdot}6 \times 10^2$	94

This reaction was followed by titrating the change in the chlorine concentration with a standard thiosulphate solution.

Temperature.	Vel. of reaction in λ = 8500 Å. k_1	Vel. of reaction in the dark. k_2	Temp. coeff. of the dark reaction.	Temp. coeff. after deducting the dark reaction in λ = 8500Å.	Quantum efficiency λ = 8500Å.
Bleaching of M/7176-*neocyanin.**					
20°	0·00112	0·00000632		1·1	0·98
30°	0·00123	—		1·04	1·65
40°	0·00128	—			2·30
6·75N-*Citric acid and* N/44·4-*chromic acid*, 10 *c.c. each.*					
24°	0·000413	0·000359	3·73	3·15	1·1
34°	0·00151	0·00134	3·65	2·90	3·2
44°	0·00534	0·00485			4·3
Decomposition of M/80·8-*sodium cobaltinitrite.**					
20°	0·000730	0·000589	3·5	3·05	0·92
30°	0·00251	0·00202	3·04	2·84	1·3
40°	0·00754	0·00632			3·9
N/250-*Ferric chloride and* N/50-*ammonium sulphocyanide*, 10 *c.c. each.*					
20°	0·000173	0·0000017		2·72	2·5
30°	0·000471	—		2·61	3·9
40°	0·00123	—			5·6
N/10-*Potassium oxalate and* N/100-*bromine*, 10 *c.c. each.*					
20°	0·000819	0·00450	5·61	4·42	23
30°	0·0419	0·0256	5·2	4·30	51
40°	0·0203	0·133			72

* These reactions were followed by a Nutting's spectrophotometer.

Temperature.	Vel. of reaction in λ = 8500Å. k_1	Vel. of reaction in the dark. k_1	Temp. coeff. of the dark reaction.	Temp. coeff. after deducting the dark reaction in λ = 8500Å.		Quantum efficiency λ = 8500Å.
N/10-*Ferrous sulphate* (8 c.c.) + N/5·6-*sulphuric acid* (2 c.c.) *and* N/100-*iodine* (10 c.c.).*						
	$k_{\frac{1}{2}}$	k_1 →	$k_{\frac{1}{2}}$	k_{40}/k_{30}	k_{40}/k_{30}	
30°	0·000903	0·000377	0·000660			5·4
35°	0·00153	0·000675	0·00113	·82	2·52	8·9
40°	0·00246	0·00112	0·00185			13·4

In presence of sulphuric acid the colour of ferric ion formed does not play any part in the optical measurements.

N/2·95-*Potassium oxalate* (10 c.c.) *and* N/11·36-*iodine* (10 c.c.).

	$k_{\frac{1}{2}}$	k_1 →	$k_{\frac{1}{2}}$			
20°	0·00185	0·00000702	0·000050	6·96	4·06	2·1
30°	0·00767	0·0000487	0·00035	6·87	3·86	5·2
40°	0·0307	0·000336	0·0024			13·1

N/4·69-*Sodium lactate* (10 c.c.) *and* N/100-*iodine* (10 c.c.).

	k_1	k_1			
20°	0·000757	0·000720	2·49	2·29	1·8
30°	0·00187	0·00179	2·31	2·13	3·4
40°	0·00431	0·00414			6·7

N/2·42-*Sodium tartrate and* N/100-*iodine*, 10 c.c. *each.*

	k_1	k_1			
20°	0·000395	0·000375	2·51	2·47	2·3
30°	0·000990	0·000948	2·49	2·38	4·2
40°	0·00246	0·00236			7·3

N/2·69-*Sodium malonate and* N/100-*iodine* ,10 c.c. *each.*

	k_1	k_1			
20°	0·00251	0·00227	2·22	2·08	1·9
30°	0·00553	0·00503	2·18	2·0	3·2
40°	0·0120	0·0110			5·2

Temperature.	Vel. of reaction in λ = 8500Å.	Vel. of reaction in the dark.	Temp. coeff. in the dark.	Temp. coeff. after deducting the dark reaction in λ = 8500Å.		Quantum efficiency in λ = 8500Å°.
			2/3N-*Sodium nitrite* (5 *c.c.*) + N/32-*iodine* (10 *c.c.*) + N/6·25-*sodium acetate* (5 *c.c.*).			
	$k_{\frac{1}{2}}$	k_1	$\longrightarrow$ $k_{\frac{1}{2}}$			
30°	0·0147	0·00319	0·0090	2·70	2·35	36
40°	0·0375	0·00366	0·0241	2·61	2·20	52
50°	0·0835	0·0226	0·0537			73
			N/5-*Citric acid* (10 c.c.) + *N*/50-$KMnO_4$ (5 c.c.) + N/69-$MnSO_4$ (5 c.c.).*			
	k_1	k_1	k_{35}/k_{25}	k_{35}/k_{25}		
15°	0·00512	0·00473				1·02
25°	0·0148	0·0138	2·92	2·56		3·13
30°	0·0232	0·0219				4·25

In the above tables k_1 represents the unimolecular velocity coefficient and $k_{\frac{1}{2}}$ the semimolecular coefficient calculated from the same experimental results carried on in the dark.

Discussion.

The experimental results show that radiations of wave-lengths 7304Å and 8500Å accelerate several photochemical reactions. From our measurements of light absorption with the help of a radiomicrometer, it is evident that radiations of wave-lengths 7304Å and 8500Å are actually absorbed by the reacting system. The molecules of the reacting system are activated by the absorption of radiation and the activated molecules then react. From our experimental results we conclude that the halogen molecules need not be atomised in order to be active, because, in the reactions involving halogens which have been studied in this paper, it cannot be assumed that the halogen molecules have been atomised. The maximum wave-length necessary to atomise the halogens are as follows:—

Chlorine, 5400Å; bromine, 6230Å; iodine, 8360Å.

All these wave-lengths are shorter than the radiation of wave-length 8500Å used in this investigation.

It is well known that in a system there are a few molecules, the energy of which is greater than the energy of the average molecules. When the incident radiation of wave-length 8500Å falls on such an active molecule, the molecule is further activated by the absorption of this incident radiation and under favourable conditions the molecule may be atomised. This view might explain the atomisation of the halogen molecules by radiations longer than that calculated from the heat of dissociation. Unfortunately no case of atomisation of a molecule has been observed in the Raman-effect. Hence we are forced to the conclusion that an atomisation of a molecule in the Raman-phenomenon is not very probable and in all the photochemical reactions in radiations of wave-lengths 7304Å and 8500Å the halogen molecules are likely to be activated and not atomised.

We have emphasised in previous publications from these laboratories that Einstein's law of photochemical equivalence mostly fails in exothermal reactions. Many molecules react per quantum of energy absorbed. It seems likely that several molecules may be activated by the absorption of one quantum. Our experimental results recorded in this paper show that with several reactions Einstein's law is applicable when illuminated by radiations of wave-length 8500Å. It appears therefore that a quantum of small energy-content can activate one or two molecules and hence in radiations of longer wave-lengths the law of Einstein will be valid.

In previous publications we have emphasised that the wave-lengths obtained by the application Perrin-Lewis hypothesis may be looked upon as the threshold limit. No appreciable acceleration of the chemical change is likely to take place with radiations of longer wave-lengths than the threshold limit.

In the following table the threshold wave-lengths are calculated from their temperature coefficients.

Reacting mixture.	Temp. coeff. ("dark").	Wave-length.
Citric acid + chromic acid.	3·73	1·20 μ
Decomposition of sodium cobaltinitrite.	3·50	1·3
Potassium oxalate + bromine.	5·6	0·94
Ferrous sulphate + iodine.	2·92	1·46
Potassium oxalate + iodine.	6·96	0·86
Citric acid + $KMnO_4$ + $MnSO_4$.	2·92	1·46
Inversion of cane sugar.	3·85	1·19
Oxalic acid + chlorine.	2·95	1·47

It is evident that the above reactions should be accelerated by short infra-red radiations and actually they are accelerated by wave-lengths 7304Å and 8500Å. It is also clear from our researches that all radiations of frequency greater than the threshold frequency calculated from the temperature coefficient are appreciably absorbed by the reacting systems and can accelerate the reactions investigated. These results support the view that radiation plays an important part in chemical reactions and our experiments strengthen the radiation hypothesis of chemical change.

Summary.

1. Sixteen reactions have been found to be accelerated by radiations of wave-length 8500Å, which lie in the infra-red region of the spectrum. Four reactions have also been studied in radiations of mean wave-length 7304Å.

2. A saturated solution of potassium dichromate placed in a cobalt-glass cell of one centimetre thickness cuts off all radiations shorter than 8000Å. This has been shown photographically.

The quantum efficiency of all these reactions increases with increase in temperature.

4. The temperature coefficients of all these reactions in radiations of wave-lengths 7304Å and 8500Å are less than those of the corresponding dark reactions.

5. Chemical changes can be accelerated by short infra-red radiations in such cases where the values theoretically obtained predict that possibility and that these radiations are appreciably absorbed by the reacting systems.

6. Our results support the view that radiation plays an important part in chemical reactions and that the halogen molecules are not atomised in these photochemical reactions.

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Adsorption by Titanium Hydroxide Sol.

By L. S. Bhatia and S. Ghosh.

Titanium hydroxide sol was first prepared by Graham (*Phil. Trans.*, 1861, **151**, 213) by adding hydrochloric acid into sodium titanate solution. Recently Majumdar (*J. Indian Chem. Soc.*, 1929, **6**, 857) has prepared the sol by dropping titanium tetrachloride in water. The free hydrochloric acid was removed by dialysis but it was found that the sol precipitated before the chloride ion was completely removed from the colloidal solution. In the investigations to be described in this paper, titanium hydroxide sol was prepared by adding titanium tetrachloride to distilled water. The mixture was kept in a bath (18°) during the precipitation and was allowed to dialyse at the room temperature. With continued dialysis the sol becomes unstable as the following experimental results for coagulation with potassium chloride and potassium sulphate will show.

Table I.

2 C.c. of the sol are taken each time.

Total volume=5 c.c. Time=½hour.

Concentration of the sol. TiO_2 per litre.	Time of dialysis in hours.	Electrolyte necessary for coagulation.		Viscosity at 30°.	p_H value.
		N/5-KCl	*N*/250-K_2SO_4.		
15·68 g.	48	2·10 c.c.	0·95 c.c.	0·00908	2·1
15·44	72	1·25	0·70	0·01042	2·5
15·26	96	0·35	0·45	0·01228	2·8
15·02	168	0·10	0·40	0·01437	3·5

The viscosities and the hydrogen ion concentrations* of the sols were also measured and are recorded in the above table. It will also be seen from our results that as the sol becomes unstable with the decreasing concentration of hydrogen ions, the ratio of the coagulating powers of KCl and K_2SO_4 diminishes and the viscosity of the sol increases. In one of our papers (*J. Phys. Chem.*, 1930, **34**, 326) we have shown that the precipitation values (P) of ions of different valencies can be expressed by the following modified equation of Whetham:

$$P_1 : P_2 : P_3 = 1 : \tfrac{1}{2}a : \tfrac{1}{3}a^2,$$

where $a = e^{-\frac{qe}{Dr}/kT}$, where q is the electrical charge on the colloid particles, e is the electronic charge, D is the dielectric constant, r the distance of double layer, T is the absolute temperature and k, the Boltzmann constant. Hence as the electrical charge on the colloid particles of titanium hydroxide sol gradually diminishes on continued dialysis, the sol becomes more and more viscous and the ratio of the coagulating powers of Cl' and SO_4'' ions gradually decreases to approach the limiting value of 1 : 2. The sol becomes very unstable when the p_H value is 4·1 and the hydroxide sets to a jelly within the parchment bag, when the dialysis of the sol is carried on further.

These results, therefore, prove that the presence of hydrogen ions is essential for the stabilisation of positively charged titanium hydroxide sol. The sol thus prepared of p_H value 3·9 was found to appreciably adsorb anions and accordingly some experiments were carried out on the adsorption of anions. For this purpose 10 c. c. of titanium hydroxide sol were taken in small Jena-glass bottles and 40 c.c. of electrolytes of various concentrations were added. The sol was coagulated and the whole mixture was thoroughly shaken and kept for 20 hours to attain equilibrium. The clear liquid at the top of the precipitate was next analysed and thus the concentration of the anion after adsorbtion was determined.

* The viscosities were measured after the method of Farrow (*J. Chem. Soc.*, 1912, 101, 347) and the hydrogen ion concentrations were determined by the indicator method using nitrophenols.

TABLE II.

Concentration of the sol=15·02 g. TiO_2 per litre.

Amount of sol taken=10 c.c. Total volume=50 c.c. Time=20 hours.

Original conc. in moles per litre.	Final conc. in moles per litre.	Amount adsorbed in millimoles per g. adsorbent.	Original conc. in moles per litre.	Final conc. in moles per litre.	Amount adsorbed in millimoles per g. adsorbent.
Adsorption of chloride ions from KCl.			*Adsorption of bromide ions from* KBr.		
0·3000	0·2920	0·2660	0·3000	0·2950	0·1660
0·2000	0·1924	0·2530	0·2000	0·1954	0·1530
0·1000	0·0936	0·2130	0·1000	0·0960	0·1330
0·0500	0·0452	0·1590	0·0500	0·0472	0·0999
Adsorption of nitrite ions from KNO_2.			*Adsorption of iodate ions from* KIO_3.		
0·0910	0·0820	0·299	0·0750	0·0737	0·0432
0·0610	0·0530	0·266	0·0500	0·0487	0·0432
0·0305	0·0240	0·216	0·0250	0·0238	0·0399
0·0153	0·0102	0·172	0·0125	0·0166	0·0299
Adsorption of hydroxyl ions from KOH.			*Adsorption of chromate ions from* K_2CrO_4.		
0·1200	0·1190	0·0302	0·0400	0·0392	0·0266
0·0800	0·0792	0·0266	0·0200	0·0194	0·0199
0·0400	0·0394	0·0199	0·0100	0·0095	0·0166
0·0200	0·0197	0·0099	0·0050	0·0047	0·0099
Adsorption of dichromate ions from $K_2Cr_2O_7$.			*Adsorption of sulphate ions from* K_2SO_4.		
0·0320	0·0295	0·0832	0·3000	0·2906	0·312
0·0213	0·0192	0·0698	0·2000	0·1912	0·292
0·0107	0·0094	0·0432	0·1000	0·0923	0·256
0·0054	0·0049	0·0166	0·0500	0·0443	0·189

Original conc. in moles per litre.	Final conc. in moles per litre.	Amount adsorbed in millimoles per g. adsorbent.	Original conc. in moles per litre.	Final conc. in moles per litre.	Amount adsorbed in millimoles per g. adsorbent.
Adsorption of thiosulphate ions from $Na_2S_2O_3$.			*Adsorption of ferricyanide ions from* $K_3Fe(CN)_6$.		
0·1430	0·1378	0·173	0·3000	0·2882	0·392
0·0950	0·0895	0·183	0·2000	0·1885	0·382
0·0475	0·0439	0·119	0·1000	0·0890	0·333
0·0238	0·0214	0·079	0·0500	0·0420	0·266

Original concentration in moles per litre.	Final concentration in moles per litre.	Amount adsorbed in millimoles per g. adsorbent.
Adsorption of ferrocyanide ions from $K_4Fe(CN)_6$.		
0·0750	0·0718	0·106
0·0500	0·0474	0·086
0·0250	0·0233	0·056
0·0125	0·0116	0·003

From the above tables and Fig. I, we find that the adsorption of different anions by titanium hydroxide sol is in the following decreasing order:

$Fe(CN)_6''' > NO_2' > SO_4'' > S_2O_3'' > Cr_2O_7'' > Br' > Fe(CN)_6'''' > IO_3' > CrO_4'' > OH'$, when the amounts of adsorption are expressed in millimoles per gram of adsorbent. We have also investigated the coagulation as well as the gelation of titanium hydroxide sol by these anions. The coagulation point has been determined by noting the appearance of flocculation in the sol after half an hour of the addition of electrolyte. It was found that the sol also sets to a jelly by the addition of electrolytes and the gelation values were determined immediately after the addition of the electrolyte. The following results were obtained:

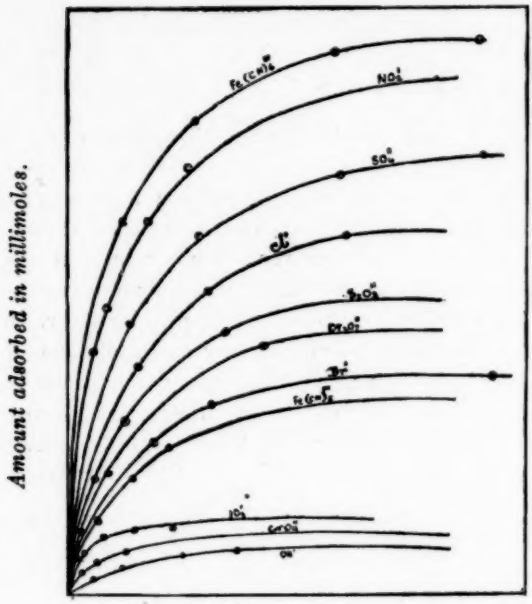

FIG. 1.

TABLE III.

Sol taken = 3 c.c. Total volume = 4 c.c. Time = ½ hour.

Electrolyte.	Precipitation values in moles.	Gelation values in moles.
KCl	0·00300	0·00350
KBr	0·00450	0·00500
KIO_3	0·00050	0·00075
KNO_3	0·00125	—
KOH	0·00013	—
$K_2Cr_2O_7$	0·00030	0·00050
K_2CrO_4	0·00040	0·00050
$Na_2S_2O_3$	0·00060	0·00100
K_2SO_4	0·00035	0·00050
$K_3Fe(CN)_6$	0·00010	0·00012
$K_4Fe(CN)_6$	0·00008	0·00009

The above table shows that the coagulating powers of the different anions were in the following decreasing order:

$Fe(CN)'_6''' > Fe(CN)_6''' > OH' > SO_4'' > Cr_2O_7'' > Cr_2O_4'' > IO_3' > S_2O_3'' > NO_2' > Cl' > Br'$.

Best jellies were obtained when the gelation was effected by monovalent electrolytes possessing low coagulating powers. The gels synerised very quickly after the addition of the electrolyte. The polyvalent anions possessing greater coagalating powers, possess a greater synerising effect. Our experimental results on the coagulating powers of the different anions by titanium hydroxide sol, show that the Schulze-Hardy law, *i.e.*, the greater the valency of an anion, the greater is its coagulating power is applicable, except in the case of OH' ion which possesses coagulating power greater than bivalent S_2O_3'' ion. It may be of interest to note that OH' ion possesses a great coagulating effect on several positively charged hydroxide sols like those of $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc.

In one of the communications (*J. Phys. Chem.*, 1926, **30**, 830) from these laboratories it has been suggested that the high coagulating power of the OH' ions for the positively charged sols stabilised by hydrogen ions is due to the removal of hydrogen ions by the introduction of OH' ions. Iodate ions also possess a greater coagulating power than that of other monovalent ions and it approaches the coagulating power of the bivalent anion S_2O_3''. Similar results have been obtained by Weiser and Middleton (*J. Phys. Chem.*, 1920, **24**, 30) with iodate ions and the positively charged sol of $Fe(OH)_3$.

We are of the opinion that this behaviour of iodate ions arises out of their tendency to remain in the polymerised condition in solution and thus the iodate ion behaves as a bivalent anion. Very recently Dhar (*J. Indian Chem. Soc.*, 1928, **5**, 585) has also come to the same conclusion from the coagulation experiments and other considerations.

It has been already shown by us that the interpretation of the Schulze-Hardy law that the greater the valency of an ion, greater is its amount of adsorption is not true (compare *J. Phys. Chem.*, 1924, **28**, 457; 1926, **30**, 628). Our experimental results on the coagulation and adsorption with titanium hydroxide sol show that the tetravalent anion $Fe(CN)_6''''$ which possesses a very high coagulating power is comparatively less adsorbed than several anions of lower valency.

Freundlich (*Kolloid Z.*, 1907, **1**, 321), Weiser (*J. Phys. Chem.*, 1925, **29**, 955) and others have assumed that greater the adsorbility of an ion, the greater will be its coagulating power. This assumption seems apparently reasonable specially with the ions of the same valency because along with the electrical attraction of the oppposite ly charged ions towards the sol particles, the chemical affinity between the sol and the coagulating ion may help in the coagulation of a, sol because we know that the greater the chemical affinity of an ion towards an absorbent the greater is its adsorbility. We have, however, shown that the experimental evidence available in this line does not support this assumption. With titanium hydroxide sol, the coagulating power of bivalent and monovalent anions are in the following decreasing order:

Monovalent anions $OH > IO_3 > NO_2 > Cl > Br$.

Bivalent anions $SO_4 > Cr_2O_7 > Cr_2O_4 > S_2O_3$.

The amount of adsorption of these bivalent and monovalent anions are in the following decreasing order:

Monovalent anions $NO_2 > Cl > Br > IO_3$.

Bivalent anions $SO_4 > S_2O_3 > Cr_2O_7 > CrO_4$.

From these experimental results, therefore, we come to the conclusion that even for the anions of the same valency greater adsorption does not necessarily result in a greater coagulating power and hence the views of Freundlich, Bancroft and Weiser are not correct.

We have found that titanium hydroxide sol preferentially adsorbs more of an anion than a cation with the liberation of OH' ions, which decreases the hydrogen ion concentration of the sol, thus the p_H value of the original sol was increased from 3·9 to 7·3 by addition of 10 c.c. of *N*-potassium sulphate solution to 10 c.c. of titanium hydroxide sol. In one of the communications (*loc. cit.*) from these laboratories it has been shown that substances like MnO_2, SiO_2 etc., adsorb more of cation than anion because of their acid character, whilst substances like $Fe(OH)_3$, $Al(OH)_3$ etc., adsorb large quantity of anions because of their basic character. Our results, therefore, confirm that titanium hydroxide sol, also known as titanic acid, is

more basic than acidic because it preferentially adsorbs a cation with liberation of OH' ions. This conclusion is further supported by the fact that OH' ions are adsorbed in very small amounts by titanium hydroxide sol.

Majumdar (*loc. cit.*) has observed that a titanium hydroxide sol becomes stable towards the action of electrolytes when it is allowed to age. We have also obtained similar results on the ageing of titanium hydroxide sol. It has been, however, shown in an investigation (compare *J. Phys. Chem.*, 1926, **30**, 1564) from these laboratories that the sols of substances like $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$ etc., have a tendency to become unstable on keeping because these substances lose their adsorption capacities on ageing and hence the adsorbed $H^{\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Cr^{\cdot\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$ ions, which are the stablisers of these sols are given out by these sols. This causes a decrease in the electric charge on the sols and consequently their stability. Whilst the sols of the substances like mastic, gum dammar, gamboge etc., become stable on keeping because these sols are hydrolysed giving out products of the hydrolysis, which are the stabilisers. Hence the content of the stabilisers increases with the age of the sol rendering them more stable. It therefore seems that the behaviour of titanium hydroxide sol, which is positively charged, is different from that of the positively charged sols like $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$ etc. We have, therefore, carried out an investigation on the ageing of the titanium hydroxide sol prepared in the cold and in the hot conditions and the following results were obtained.

TABLE IV.

(Sol prepared at 18°.)

Concentration of the sol = 14·3 g. of TiO_2 per litre.

Date.	Electrolyte necessary to coagulate in c.c. $N/20$-KCl	$N/500$-K_2SO_4	Viscosity at 30.	Sp. conductivity ($\times 10^{-4}$).
2.8.1929	0·85	0·75	0·01188	2·35
9.8.1929	0·95	0·75	0·01163	2·28
16.8.1929	1·00	0·80	0·01152	2·24
23.8.1929	1·05	0·80	0·01149	2·22
30.8.1929	1·05	0·82	0·01145	2·20
6.9.1929	1·05	0·80	0·01147	2·20

TABLE V.

(Sol prepared at 55°.)

Concentration of the sol = 9·22 g. TiO_2 per litre.

Date	Electrolyte necessary to coagulate in c.c. N/20-KCl	N/500-K_2SO_4.	Viscosity at 30°.	Sp. conductivity (10^{-4}).
5. 8. 29	0·45	0·50	0·00963	3·12
12. 8. 29	0·45	0·50	0·00967	3·16
19. 8. 29	0·40	0·50	0·00967	3·16
26. 8. 29	0·40	0·45	0·00978	3·17

Our results with the sol of titanium hydroxide sol prepared at 18° show that it (i) becomes stable towards its coagulation by electrolytes like KCl, K_2SO_4, (ii) shows a decrease in the electrical conductivity and (iii) a decrease in the viscosity on ageing. On the other hand a sol of titanium hydroxide prepared at 55° does not show any change in the stability and the specific conductivity and the viscosity increases very little on ageing.

It has been shown in one of our publications (*Kolloid* Z., 1929, **48**, 43) that the viscosity of a sol increases with the decrease of its electrical charge, whilst the viscosity of the sol decreases with the increase of its electrical charge. Consequently, a decrease in the viscosity of titanium hydroxide sol (prepared at 18°) on ageing shows that the sol is more electrically charged and, therefore, becomes more stable towards its coagulation by electrolytes on ageing. That the electrical charge increases with age can also be shown from the fact that the ratio of the precipitation values of monovalent anion Cl' and bivalent anions SO''_4 increases on keeping the sol prepared at 18°. On the other hand, the sol prepared in the hot condition bacomes more viscous on ageing which shows that it gets less electrically charged and hence has a tendency to become unstable. We are, therefore, of the opinion that a sol of titanium hydroxide prepared in the cold becomes stable on keeping as the free HCl present in the sol gradually acts on $Ti(OH)_4$ forming $TiCl_4$ which gives out Ti'''' ions that are completely adsorbed by the sol and hence possesses greater stabilising influence than $H^{\cdot}$ ions. A determination of the electrical conductivity of the sol prepared in the cold shows that the $H^{\cdot}$ ions are removed from the sol

by the process of ageing. This is, however, not possible with a sol prepared at 55° as it is well known that the chemical activity as well as the power of adsorption by a precipitate is considerably diminished when it is prepared in the hot condition. These conclusions are further supported from our measurements of the specific conductivity of the sol.

Summary and Conclusion.

(1) A sol of titanium hydroxide prepared by dropping $TiCl_4$ slowly into water at 18° cannot be completely freed from HCl by dialysis. It was found that the sol containing 15·2 g. TiO_2 per litre on prolonged dialysis gradually became viscous and as soon as the p_H value was more than 4·1 the whole mass coagulated as a gelatinous precipitate.

(2) The sol prepared at 18° adsorbed appreciable amounts of anions from different sodium or potassium salts and they are adsorbed in the following decreasing order:

$Fe(CN)_6''' > NO'_2 > SO''_4 > Cl' > S_2O_3'' > Cr_2O''_7 > Br' > Fe(CN)_6'''' > IO'_3 > CrO''_4 > OH'$; the amounts of adsorption are expressed in moles per gram adsorbent.

The coagulating powers of different anions are in the following decreasing order:

$Fe(CN)_6'''' > Fe(CN)_6''' > OH' > SO_4'' > Cr_2O_7'' > Cr_2O_4'' > IO_3' > S_2O_3'' > NO'_2 > Cl' > Br'$.

(3) The above results show that the generally accepted view that an ion which is highly adsorbed also possesses a high coagulating power is not supported by experiments.

(4) The amount of adsorption of OH' ions by titanium hydroxide sol is very small. The high coagulating power of OH' ions is due to the removal of the stabiliser $H^{\cdot}$ ions by OH' ions.

(5) Titanium hydroxide sol adsorbs more of an anion than a cation, with the liberation of OH' ions which increases the p_H value of the sol.

(6) We are of the opinion that titanium hydroxide (also known as titanic acid) possesses more of basic character than acidic.

(7) A sol of titanium hydroxide containing 15·2 g. TiO_2 per litre and prepared at 18° becomes stable towards its coagulation by electrolytes, shows a decrease in the specific conductivity and the viscosity on ageing.

(8) On the other hand a sol of titanium hydroxide containing 10·2 g. TiO_2 per litre and prepared at 55° does not show any change in stability and the specific conductivity and the viscosity increase very slightly on ageing.

(9) We are of the opinion that a sol of titanium hydroxide prepared in the cold becomes stable on keeping as free HCl present in the sol gradually acts on $Ti(OH)_4$ forming $TiCl_4$, which gives out $Ti^{\cdots\cdot}$ ions that are completely adsorbed by the sol and hence possess greater stabilising influence than $H^{\cdot}$ ions. This is not possible in the case of the sol prepared at 55° as it is well known that chemical activity as well as power of adsorption of a precipitate is considerably diminished when prepared in the hot condition.

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A Critical Study of Kohlschütter's Method of Preparing Silver Hydrosol.

By M. Raman Nayar and P. S. MacMahon.

In an attempt to study the oxidizability of silver under various conditions we had occasion to prepare colloidal silver by reduction of silver oxide with hydrogen, a method described for the first time by Kohlschütter (*Z. Elektrochem.*, 1908, **14**, 49). Among other things he obtained sols of varying colours such as yellowish-brown, red, reddish-violet, blue, etc. He could not control their production nor could he produce them at will. He believed that the material of the reaction vessel affected the velocity of the reaction and also the colour of the sol. The difference in appearance was not to be attributed to the dissolved glass.

Kohlschütter's sol always contained a certain amount of electrolyte namely silver hydroxide which he said could be removed by further reduction with hydrogen in a blackened platinum dish without affecting the concentration of the colloid. The colloid particle also contained a certain proportion of oxide. "The proportion in which the oxide and silver stand in the real colloid is determined by the walls of the vessel in which the reduction is carried out ; it determines on the other hand the colour of the sol. The quantity of the combined oxide in the colloid is greater and fairly uniform in the yellowish-brown sols from soft glass and quartz vessels, it is smaller and very varying in the 'variegated' sols."

Pauli and Erlach (*Kolloid Z.*, 1924, **34**, 213) have repeated Kohlschütter's experiments and come to the conclusion that with pure silver oxide, pure hydrogen and conductivity water no sol is produced. A trace of alkali or sulphide (?) ions is necessary for the formation of the sol. In Kohlschütter's experiments the alkali must have been present in the silver oxide used, and the sulphide in the hydrogen from the Kipp.

Kohlschütter's assumption that the colloid particle is not affected by Pt-H treatment is questioned by Pauli, as also the alleged relation

between the material of the reaction vessel and the colour of the sol. Pauli proposes the constitution for the colloid particle to be either (AgO, $5Ag_2O$) or [$Ag(SH)_2$, $4Ag_2O$]. The experimental basis for the formulae is not clear from Pauli's paper.

Some of our experiments had been conducted before Pauli's paper appeared, but our observations did not tally with those of Pauli, even though the experimental conditions were similar and the reagents had gone through the same processes of purification (*Proc. Indian Science Congress, Lahore*, 1927, p. 171).

Since then we have discovered the cause of the discrepancy which we believe is of importance in the theory of the formation of silver sol.

In our experiments we took every reasonable precaution in preparing pure materials and shutting out impurities. Since Pauli's theory requires the presence of traces of electrolytes, *e.g.*, alkali ions, which may be expected to be present in the silver oxide prepared chemically, it was desirable to have a perfect method of obtaining pure silver oxide. Such a method was found in the electrolysis of conductivity water with silver electrodes which yields a mixture of silver oxide and silver free from all impurities (*vide*, Nayar and MacMahon, *J. Indian Chem. Soc.*, 1930, **7**, 589).

The conductivity water employed by us had a value of K that ranged between $1{\cdot}5$ and 3×10^{-6} mhos. That the hydrogen was pure and contained no soluble impurities was shown by passing it into water for two hours or more and determining the conductivity of water before and after treatment with hydrogen.

Conductivity of water before treatment with hydrogen $= 2{\cdot}240 \times 10^{-6}$ mhos.

" " after " (2 hours) $= 1{\cdot}766 \times$ "

The conductivity had actually become less due to displacement of dissolved carbon dioxide by the hydrogen.

We used mainly silica vessels (flasks, beakers and tubes). For the repetition of Pauli's experiments Jena glass flasks were also used. All were thoroughly steamed before starting an experiment.

Repetition of Pauli's Experiments.—Pauli and Erlach after a series of experiments have come to the conclusion that with pure silver oxide, pure hydrogen and conductivity water no sol is formed. The purer the hydrogen the more difficult it is to obtain the sol. All

their experiments were devised with a view to improve the purity of hydrogen. The larger the number of washing bottles used for removing the impurities the longer the time taken for the formation of the sol. Thus with Kipp hydrogen and employing six washing bottles containing $CuSO_4$, $KMnO_4$, $HgCl_2$, H_2SO_4 and Ag_2O respectively, the sol is not formed in 30 hours. Even under the worst conditions (commercial sulphuric acid, pure zinc in the Kipp, and only one washing bottle containing pure sulphuric acid) they obtained a thick sol in 8 hours. On the other hand employing electrolytic hydrogen and two spiral washing bottles with sulphuric acid the sol was not formed even after 72 hours.

We repeated the two sets of experiments but could not reproduce the above results. The Kipp contained pure sulphuric acid (Kahlbaum) diluted with distilled water, pure zinc and a few drops of pure copper sulphate solution to start the reaction. The washing bottles contained the same reagents mentioned above, belonging to Kahlbaum's analytical or pure grade excepting silver oxide which we prepared by the precipitation of silver nitrate with caustic soda, the former being used in slight excess. In this case the washing was done by decantation until brucine test failed to give any indication of nitrate, the final washing being done with conductivity water. The reaction vessel was a silica flask kept in a water-bath maintained approximately at 60°. The inlet tube for hydrogen was of silica. Air contamination was avoided by dipping the outlet tube from the reaction vessel in a beaker of distilled water. In 15 to 20 minutes from the commencement of the experiment a yellow colour was produced inside the flask. In one hour a wine-red sol, and in two hours a fairly thick sol was obtained. The experiment was conducted for five hours per day and the supernatant liquid, namely the sol, was decanted off and fresh conductivity water added each day. After 131 hours' reduction it was found that the oxide at the bottom of the vessel had been completely reduced and no more sol produced. The colour of the sol was generally wine-red by transmitted light and grey or greenish grey by reflected light. Occasionally a bluish or sometimes a pink sol was obtained, especially towards the close of the reduction. These sols were not so stable as the red ones, but coagulated in about four weeks. The above experiments were conducted with chemically prepared silver oxide. The following table refers to a repetition of the experiment with electrolytic oxide.

TABLE I

Duration (hrs.).	Colour and remarks.	Duration (hrs.).	Colour and remarks.
1	Orange-red.	6	Reddish, not deep.
3	Deep red.	5	Orange-red.
6	Deep red.	4	Yellowish-white, faintly pink by transmitted light.
7	Brownish-red.	7	Yellowish-white.
2	Orange-red.	4½	No sol.
3	Orange-red.	4	No sol; no more oxide left; residue pure silver.

The following tests were applied for the detection of oxide in the silver residues:

(1) The residue was shaken well with water and to the clear liquid hydrochloric acid was added. No opalescence, showing the absence of oxide.

(2) Residue was treated with a concentrated solution of KCl in a clean platinum or porcelain dish. A drop of phenolphthalein was added and the tint, if any, compared with a blank test. No red coloration was produced indicating the absence of oxide. This test was found to be exceedingly delicate for the detection of any trace of silver oxide.

Experiments with Silver-coated flasks.—Pauli carried out his experiments in silver flasks, and his conclusions were based upon results obtained from these, even though he said the same results were obtained with Jena glass flasks. Our experiments in silica and Jena glass flasks gave results contradictory to Pauli's experiments. The only part of Pauli's experiment which we could not repeat was the employment of silver flasks. In the course of our work, especially on continuous reduction of silver oxide without change of water, the reaction flask became coated with a beautiful mirror of silver. This approximated to Pauli's silver flask. Pauli also attempted some experiments in silvered flasks, but dismissed them as unsatisfactory.

In an experiment which had inadvertently been allowed to go on, it was found that a very thick greyish-white sol had been produced and the walls of the flask had a beautiful coating of silver mirror. When the liquid was replaced by fresh conductivity water no sol was produced, even though the residue at the bottom of the

flask gave tests for the presence of oxide. This put us on the right track for the explanation of the contradictory results, and some attempts were made to elucidate this phenomenon.

A Duro-glass flask was silvered inside by reduction of silver tartrate. On steaming it was found that scales of silver were coming off. To remove the alkali contamination, after the usual washing, the flask was filled with water and heated, at the same time a current of hydrogen was bubbled through for some hours. This flask was used for the next experiment.

TABLE II.

Silvered glass flask: Electrolytic silver oxide.

Duration. (hrs.).	Colour and remarks
6	White sol.
20	Thick yellowish-white sol.
	(Sol replaced by conductivity water.)
7	No sol produced.

The residue gave the phenolphthalein test for the presence of silver oxide. Similar results were obtained with chemically prepared silver oxide.

TABLE III.

Fresh silica flask: Chemically prepared silver oxide.

Duration (hrs.).	Colour and remarks.
8	Usual yellow colour in 15 minutes, red sol in 2 hours and thick milk-white sol in 8 hours.
18	Thin white sol and mirror.
	(Sol replaced by fresh water.)
10	Thick white sol.
	(Sol replaced by fresh water).
16	White sol.
	(Sol replaced by fresh water).
16	No sol.

The residue still contained oxide. The white sol was always unstable.

Silvered and Nonsilvered Silica flasks: Chemically prepared Silver Oxide.—That silvered surface has a negative catalytic effect is definitely proved by the following experiments:

(*i*) Silver oxide was reduced in a fresh silica flask continuously for 29 hours, when a mirror was formed and a thick yellowish-white sol was obtained. (This sol was kept aside when most of it settled down leaving a pale white supernatant liquid).

(*ii*) The sol was replaced by fresh conductivity water and reduction continued for another 4 hours. On examination a very faint white sol was found indicating that it was very unstable.

(*iii*) The residue was transferred to a fresh silica flask and reduction carried out for 3 hours only. The normal reddish sol was produced.

This conclusively shows that while silver oxide residue *in a silvered flask* produces a thin white unstable sol, in *unsilvered flask* the same residue produces the normal stable sol, proving thereby that the silver surface has a negative catalytic effect. (In the earlier experiments whenever the silver mirror was formed it was always removed by treatment with nitric acid followed by steaming.) That the material of the reaction vessel affected the velocity of reaction and the colour of the sol was also the opinion of Kohlschütter.

Further Observations on the Properties of the Sol.—In the course of our work we had occasion to prepare the sol under varying conditions which did not corroborate the following statement in Mellor's "Treatise on Inorganic Chemistry," Vol. 3, pp. 555-6, evidently extracted from Kohlschütter's paper:—"Walls of soft glass or quartz give yellowish-brown hydrosols..... In 8 to 10 hours between half and one litre of intensely coloured sol is obtained. At temperatures below 50° the reduction is too slow; above 60° the sol is unstable."

We, on the other hand, usually obtained a wine-red sol (in transmitted light) in a quartz flask. The time required was only two to three hours. In less than an hour from the commencement of the experiment, the liquid becomes yellowish in colour and in two hours a deep red coloured sol is formed, especially if the experiment is started with fresh materials. The temperature of formation if not so well defined as stated above. The sol is formed even at 25°. The sixth washing bottle containing silver oxide employed for washing Kipp hydrogen (*vide supra*) was found to contain silver sol at the end of the experiment in one day, that is, in five hours. On the other

hand, the sol is certainly not unstable above 60°. When once formed, it could be boiled without coagulation, provided there was no solid matter at the bottom of the vessel. Further, the sol is formed readily at temperatures above 60°; our working temperature was usually 70-80°. The sol so produced was quite stable.

It was suggested that dialysis of such a sol (produced at the higher temperature) would result in coagulation. This had not been our experience either. We again prepared the sol at 80-85° (chemically prepared silver oxide, water of $K = 1{\cdot}38 \times 10^{-6}$ mhos) in silica flask by reduction for 3 hours. The colour was red by transmitted light and greenish grey by reflected light. Dialysis was carried out in Pauli's folded dialyser (parchment paper) in a paraffined rectangular trough protected from atmospheric contamination by a paraffined glass cover. The course of dialysis was observed by conductivity determinations. The liquid outside the dialyser was changed every day.

Conductivity of sol on 1st day : $K_{1\,0} = 23{\cdot}66 \times 10^{-6}$ mhos.

,, 18th ,, $K_{2\,5} = 3{\cdot}298$,,

,, water outside dialyser : $K_{2\,5} = 2{\cdot}587$,,

This sol was kept aside. Even after 18 months there was no coagulation. The concentration of the sol was found to be 0·0205 g. of Ag per litre. If the reduction of AgOH solution is carried on at the boiling point a coarse suspension results, which easily settles down to the bottom of the vessel.

Discussion.

Pauli in his first paper on Kohlschütter sol comes to the conclusion that a certain minimum amount of alkali ions is necessary before the silver sol can be produced, which he has incorporated in his "complex" theory of the mechanism of the sol formation. Silver oxide can dissociate in two ways:

$$2\,Ag_2O \rightleftharpoons (Ag_3O)^{\cdot} + (AgO)' \quad \ldots \quad (1)$$

$$AgOH + Ag_2O \rightleftharpoons (Ag_3O)^{\cdot} + (OH)' \quad \ldots \quad (2)$$

The strong basic properties of the solution of silver oxide suggests that equation (2) predominates. But only (1) is capable of giving negative complex ions, even though according to the Law of Mass Action, the formation of appreciable quantities of these negative ions offers little probability. The trend of Pauli's argument is that the

presence of the large volumed alkali ion favours equation (1) by supplying the positive contra ions ("Gegenionen"), and in the absence of alkali ions no sol is to be expected. When once the sol is produced the alkali ions may be replaced by $H^{\cdot}$ ions by dialysis, which then gives rise to what Pauli calls an "azidoide." The dialysed silver sol is a very dilute acid or a "secondary azidoide."

The defect of this really complex theory is that Pauli's own experiments contradict it. Stable Bredig sol is produced in pure AgOH solution, containing no alkali ions (Pauli and Perlak, *Kolloid Z.*, 1926, **39**, 195). Our own observations are in contradiction to Pauli and Erlach's experiments on Kohlschütter sol. With silver oxide prepared chemically as well as electrolytically, pure hydrogen and conductivity water and thoroughly washed and steamed silica and Jenaglass vessels, we always obtained the Kohlschütter sol. The only time when we did not get the sol was when silvered vessels were used. The silver flasks used by Pauli must be presumed to have a negative catalytic effect. (Pauli however says that he obtained similar results—non-production of sol in Jena-glass vessels also, especially after long use).

Instead of this round-about method of explanation, the dissociation of silver oxide may be pictured as:

$$Ag_2O \rightleftharpoons Ag^{\cdot} + (AgO)' \qquad (1)$$

besides

$$AgOH \rightleftharpoons Ag^{\cdot} + (OH)' \qquad (2)$$

where the $Ag^{\cdot}$ ions may be displaced by $H^{\cdot}$ ions in the process of reduction by hydrogen (*cf.* electromotive series of elements), and the negative ion $(AgO)'$, becomes the condensation centre for the formation of the colloid particle. The presence of alkali may favour this, but it is not essential. That silver oxide can behave as an amphoteric oxide has been shown by the work of Eric Laue (*Z. anorg. Chem.*, 1927, **165**, 325). The presence of a stronger alkali may suppress or reverse the ionization (2) and hence favour equation (1). Thus the alkali may be expected to facilitate the formation of the sol. The centre of importance then would be shifted from the alkali ion to the hydroxyl ion.

The catalytic effect (negative in this case) of the silver surface may perhaps be attributed to the electromotive behaviour of the metal. It is well known that a silver electrode is electrically posi-

tive with respect to a solution containing silver ions. A silver surface then has the same effect as an increase in the concentration of $Ag^{\cdot}$ ions near the walls of the vessel, where apparently the reaction is taking place. This would result in the reversal of equation (1) and hence the absence of the necessary condensation centre for the formation of the colloid particle.

A silica or glass surface cannot be expected to behave similarly to silver. At the worst the former can only be indifferent to the chemical reaction taking place in its neighbourhood; but probably it helps the reaction catalytically, *i.e.*, behaves as a positive catalyst. Pauli's experimental observation that Jena glass vessels behave similarly to silver requires confirmation. Our experiments contradict it.

Summary.

(1) For the formation of Kohlschütter sol the presence of alkali ions is not essential as stated by Pauli. The walls of the experimenting vessel determine the nature of the sol. Silvered vessels produce no sol or only thin pale white unstable sols. Silica or glass vessels invariably give rise to wine-red stable sols.

(2) The contradiction between Pauli's experimental results and ours on Kohlschütter sol has been traced to the negative catalytic effect of silver, of which material the former's experimenting vessels were made.

(3) Stable Kohlschütter sol has been prepared at 85°. Reduction of silver oxide solution near the boiling point produces a coarse suspension.

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The Photochemical Reaction between Sodium Nitrite and Iodine.

By A. K. Bhattacharya and N. R. Dhar.

This reaction is very sensitive to light and has been investigated in detail in these laboratories (Banerji and Dhar, *Z. anorg. Chem.*, 1924, **134**,172; Mukerji and Dhar, *J. Phys. Chem.*, 1929, **33**, 850). The velocity of the reaction has been followed by measuring the changes in the concentration of iodine against thiosulphate solution. Recently Berthoud and Berger (*J. Chim. phys.*, 1928, **25**, 562) has shown that nitrite and iodine react more readily in presence of sodium thiosulphate solution and consequently the estimation of iodine by thiosulphate leads to erroneous results.

In this communication we are submitting the results obtained in the determination of the order, temperature coefficient and quantum efficiency of this reaction in light of different wave-lengths. We have determined the changes in the concentration of iodine by a Nutting's spectrophotometer.

The reaction can be represented by the equation:

$$NaNO_2 + I_2 + H_2O \rightleftharpoons 2HI + NaNO_3.$$

The influence of the variation of intensity of the incident radiation has been investigated in different radiations and using different amounts of potassium iodide. which is a marked retarder. Both sodium acetate and borax solutions have been used as buffer solutions.

Kinetics and Quantum Efficiency.

The source of light and the experimental arrangement are the same as described in a previous paper (Bhattacharya and Dhar. *Z. anorg. Chem.*, 1928, **176**, 372).

The following are the experimental results:—

2/3 *N*-Sodium nitrite = 5 c. c.; *N*/32-iodine in *N*/8·2- potassium iodide = 10 c. c., in presence of 5 c. c. *N*/6·25-sodium acetate.

Condition.	Temperature.	Monomolecular k_1.	Semi-molecular $k_{\frac{1}{2}}$. After deducting the dark reaction.	Temp. coeff.	Temp. coeff. after deducting the dark reaction.	Quantum efficiency.
Dark	30°	0·00319		2·7		
		$k_{\frac{1}{2}}$ 0·0090				
	40°	0·00866		2·61		
		$k_{\frac{1}{2}}$ 0·0241				
	50°	0·02260				
		$k_{\frac{1}{2}}$ 0·0537				
$N/3$-$NaNO_2$	30°	0·00162		2·59		
	40°	0·00419		2·49		
	50°	0·0104				

Hence the order of the reaction is bimolecular in the dark.

$\lambda = 4725$Å	30°	$k_{\frac{1}{2}}$ 0·0251	0·0161			$5·15 \times 10$
	40°	0·0575	0·0334	2·07		8·6 ,,
	50°	0·1207	0·0670	2·0		11·9 ,,
$\lambda = 5650$Å	30°	0·0212	0·0122			3·94 ,,
	40°	0·0510	0·0269	2·2		6·8 ,,
	50°	0·111	0·0563	2·1		10·2 ,,
$\lambda = 7304$Å	30°	0·0186	0·0096			3·8 ,,
	40°	0·0461	0·0220	2·29		6·2 ,,
	50°	0·101	0·0473	2·15		8·1 ,,
$\lambda = 8500$Å	30°	0·0147	0·0057			3·6 ,,
	40°	0·0375	0·0134	2·35		5·2 ,,
	50°	0·0835	0·0298	2·20		7·3 ,,

From the foregoing results it will be observed that Einstein's law of photochemical equivalence is not exactly applicable to this reaction. The quantum efficiency increases with temperature and the frequency of the incident radiation. Similar results have been obtained with numerous other reactions.

The experimental results show that the temperature coefficients of the photochemical changes are less than those of the corresponding thermal reactions. The greater the acceleration in light of different wave-lengths, the less the temperature coefficient. Another

interesting fact is that the temperature coefficient of the purely light reaction is much greater than unity. Similar results have been obtained with several other reactions so far investigated in these laboratories. Hence we are in a position to uphold our view that the temperature coefficient of p hotochemical reactions need not be unity and depends on the acceleration of the light reaction in comparison with the dark reaction (compare Dhar, *J. Chem. Soc.*, 1917, **111**, 707). Many people believe that the photochemical reactions are brought about by violet and ultra-violet radiations only. Our experimental results, however, prove that this and several other reactions can be accelerated by radiations of wave-length 7304Å and 8500 Å which lie in the infra-red region of the spectrum. Moreover, we have shown that these radiations are actually absorbed by the reacting substances.

Relation between Absorption of Light and Velocity.

The experimental arrangements are the same as described in previous paper (Bhattacharya and Dhar, *Z.anorg. Chem.*, 1928, **175** 375).

The corresponding dark reaction was always substracted from the light reaction before calculating the effect of intensity of light on the velocity of this reaction.

The following are the experimental results :—2/3*N*-sodium nitrite=5 c. c. ; *N*-32-iodine in presence of 5 c. c. 6·25*N*-sodium acetate=10 c. c. Temperature=40°.

Diameter of the aperture.	Semi-molecular. $k_{\frac{1}{2}}$	Semi-molecular reaction in light after deducting the dark reaction $k_{\frac{1}{2}}$.	
	A. Source.—*Sunlight*. $k_{\frac{1}{2}}$ (dark)=0·0241		
2 cm.	0·256	0·2319	(I
0·8	0·169	0·1449	(II)
0·4	0·143	0·119	(III)
	B. Source.—1000-*watt lamp*.		
2	0·0886	0·0645	(I)
0·8	0·0556	0·0315	(II)
0·4	0·0416	0·0175	(III)

Diameter of the aperture.	Semi-molecular. $k_{\frac{1}{2}}$	Semi-molecular reaction in light after deducting the dark reaction $k_{\frac{1}{2}}$.
	C. Region.— $\lambda = 5650$Å	
2 cm.	0·0460	0·0219 (I)
0·8	0·0296	0·0055 (II)
0·4	0·0259	0·0018 (III)
	D. Region.— $\lambda = 7304$Å	
2	0·0420	0·0179 (I)
0·8	0·0277	0·0036 (II)
0·4	0·0251	0·0010 (III)
	E. Region.— $\lambda = 7304$A	

$N/32$—Iodine dissolved in 0·75 g. KI in presence of $N/105$-borax solution.

		$k_{\frac{1}{2}}$ (dark) = 0·0450
2	0·0592	0·0142
0·8	0·0471	0·0021

The following results show that the absorption of radiation is approximately proportional to the intensity of the incident radiation. Temperature = 40°.

Diameter of the aperture.	Substance.	Deflection.	Difference in deflection.
2 cm.	(*i*) Distilled water	38·6 cm.	3·6 cm.
	(*ii*) Reacting mixture	35·0	
0·8	(*i*) Distilled water	21·2	0·6
	(*ii*) Reacting mixture	20·6	
0·4	(*i*) Distilled water	12·65	0·15
	(*ii*) Reacting mixture	12·5	

Ratio of intensity.	Ratio of absorption.
$\frac{3·14}{0·5024} = 6·25$	$\frac{3·6}{0·6} = 6$
$\frac{0·5024}{0·1256} = 4$	$\frac{0·6}{0·15} = 4$
$\frac{3·14}{0·1256} = 25$	$\frac{3·6}{0·15} = 24$

	Ratio of velocities.	If directly proportional to the absorption of incident radiation.	If proportional to the square root of the absorption of incident radiation.
A.	$\frac{I}{II} = \frac{0{\cdot}2319}{0{\cdot}1449} = 1{\cdot}6$	6	2·45
	$\frac{I}{II_I} = \frac{0{\cdot}1449}{0{\cdot}119} = 1{\cdot}22$	4	2
	$\frac{I}{III} = \frac{0{\cdot}2319}{0{\cdot}119} = 1{\cdot}95$	24	4·9
B.	$\frac{I}{II} = \frac{0{\cdot}0645}{0{\cdot}0315} = 2{\cdot}05$	6	2·45
	$\frac{II}{III} = \frac{0{\cdot}0315}{0{\cdot}0175} = 1{\cdot}8$	4	2
	$\frac{1}{III} = \frac{0{\cdot}0645}{0{\cdot}0175} = 3{\cdot}7$	24	4·9
C.	$\frac{I}{II} = \frac{0{\cdot}0219}{0{\cdot}0055} = 4$	6	2·45
	$\frac{II}{III} = \frac{0{\cdot}0055}{0{\cdot}0018} = 3$	4	2
	$\frac{I}{III} = \frac{0{\cdot}0219}{0{\cdot}0018} = 12$	24	4·9
D.	$\frac{I}{II} = \frac{0{\cdot}0179}{0{\cdot}0036} = 5$	6	2·45
	$\frac{II}{III} = \frac{0{\cdot}0036}{0{\cdot}0010} = 3{\cdot}6$	4	2
	$\frac{I}{III} = \frac{0{\cdot}0179}{0{\cdot}0010} = 17{\cdot}9$	24	4·9
E.	$\frac{I}{III} = \frac{0{\cdot}0142}{0{\cdot}0021} = 6$	6	2·45

Discussion.

The experimental results show that the relation between the absorption or intensity and the velocity of the reaction varies from approximately one-fourth to more than proportional. Hence it is clear that the relation between light absorption or intensity and

velocity of one and the same reaction can be varied considerably. It depends entirely on the ratio of the velocities of the light and dark reactions.

When the velocity of the thermal reaction is less and the reaction mixture is exposed to sunlight, the relation between light absorption or intensity and the velosity tends to be less than 1/3. This relation goes on increasing as the acceleration of the light reaction over the corresponding thermal reaction is decreased. It increased so much as to show a relatton approximately 3/2 in the region $\lambda = 7304$Å using $N/105$-borax solution as a buffer solution, which markedly accelerates the dark reaction. The source of light is not intense in this case. The total result is that the acceleration due to light is not marked in comparison with the dark reaction and the ratio between light absorption or intensity and velocity rises appreximately to 3/2.

These results are in entire agreement with our conclusions that the reaction between light absorption or intensity and velocity of a reaction can be varied considerably and is controlled by the ratio of the light and dark reactions.

The Influence of Sodium Nitrite on the amount of Sodium Thiosulphate necessary to react with Iodine.

The following are the experimental results:—$NaNO_2 = N/5$ + Iodine $= N/10$ (approximately). Sodium thiosulphate $= N/10$.

Vol. of iodine solution	...	10 c.c.	10 c.c.	10 c.c.	10 c.c.
Vol. of nitrite solution	...	Nil	10	20	30
Vol. of thiosulphate solution	...	9·65	8·55	6·90	6·50

Hence the titration by sodium thiosulphate is vitiated only by concentrated solutions of sodium nitrite. With the concentrations used by Banerji and Dhar (*loc. cit.*), the experimental results appear not to be vitiated by the induced reaction between nitrite and iodine due to the interaction of the latter with sodium thiosulphate.

Moreover, the results obtained in this communication using a Nutting's spectrophotometer, are in agreement with those obtained by Banerji and Dhar (*loc. cit.*) and Mukerji and Dhar (*loc. cit.*).

We are at present investigating this reaction in ultra-violet radiations and the equilibrium involved in the oxidation of nitrite ion to nitrate ion by iodine.

Summary.

1. The reaction between sodium nitrite and iodine is bimolecular in the dark. The temperature coefficient of the dark reaction is 2·7 between 30° and 40°.

2. The temperature coefficients of the light reaction are 2·07 ($\lambda = 4725$Å), 2·20 ($\lambda = 5650$Å), 2·29 ($\lambda = 7304$Å), 2·35 ($\lambda = 8500$Å) between 30° and 40°.

3. The quantum efficiency of this reaction varies from $3{\cdot}6 \times 10$ to $11{\cdot}9 \times 10$ at different temperatures and in different radiations.

4. The ratio of light absorption or intensity of the incident radiation and the velocity of the reaction can vary from approximately one-fourth to more than proportional depending on the ratio of the velocities of the light and dark reactions.

5. The titration of iodine by sodium thiosulphate in presence of sodium nitrite is only erroneous when the concentration of sodium nitrite solution is great.

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Photochemical Reduction of Tungstic and Molybdic Acids.

By S. Ghosh and A. K. Bhattacharya.

Several years ago, Wassiljewa (*Z. wiss. Phot.*, 1913, **12**, 1) observed that freshly prepared sol of tungstic acid could be reduced to the blue coloured lower oxide by reducing agents like ethyl alcohol, glucose, formaldehyde, etc., when exposed to sunlight. He found that the photochemical activity of tungstic acid sol towards reduction decreases as the sol is allowed to age and it can be regained by heating the sol to a higher temperature. Freundlich ("Kapillar, Chemie" 1922, p. 872) attributes this behaviour of tungstic acid sol to the difference in the degree of hydration of the colloidal particles with the age of the sol. In previous papers (*J. Phys. Chem.*, 1929, **33**, 1905; *Z. anorg. Chem.*, 1929, **184**, 135) we have investigated the ageing of the sols of tungstic and molybdic acids and have concluded that these sols when freshly prepared contain a large proportion of these substances in the molecular condition (simple or aggregated) and the following equilibrium exists in the sol:

$$\text{Simple molecules} \rightleftharpoons \underset{\text{molecules}}{\text{Aggregated}} \rightleftharpoons \text{Colloidal particles.}$$

We have shown that when the sols of molybdic and tungstic acids are kept at the room temperature, more and more of aggregated molecules and colloidal particles are formed at the expense of simple molecules. We have remarked in the above communications that the decrease in the photochemical activity of tungstic acid sol with time can be more fully explained by assuming that most of the tungstic acid present in the molecular condition polymerises into larger molecules or to colloidal particles, which are not chemically active as the simple molecules.

In this paper we have investigated the photochemical reduction of molybdic acid sol, freshly prepared and aged into the lower oxide, with a view to examine if similar behaviour is developed in the

case of molybdic acid, as observed by Wassiljewa with tungstic acid sol. We have already shown that the different monovalent cations exert a coagulating effect on the sols of molybdic and tungstic acids and are in the following decreasing order $Rb^{\cdot} > NH_4^{\cdot} > K^{\cdot} > Na^{\cdot} > Li^{\cdot}$.

Accordingly we have carried out some experiments on the photochemical reduction of tungstic and molybdic acid sols in the presence of these monovalent cations in amounts insufficient to cause complete coagulaion.

Sols of tungstic and molybdic acids were prepared by adding equivalent amounts of hydrochloric acid to solutions of sodium tungstate and ammonium molybdate, ethyl alcohol being used as the reducing agent.

The reacting mixtures with different electrolytes were contained in test tubes, kept in a thermostat, the temperature of which was maintained within $\pm 0{\cdot}1$ and exposed to sunlight.

The development of colour was followed by a Nutting's spectrophotometer. To isolate any particular region of the spectrum for case of comparison, a shutter red eye-piece was employed. The source of light was a 100 c.p. point-o-lite lamp working at 220 volts. Two similar neutral-tint glass cells with optically plane parallel ends were used—one for the solution whose extinction coefficient had to be observed and the other for an equal volume of distilled water so that the comparison might be made under identical conditions of original light intensity.

The time taken in the actual reading of the scale after the comparison of the two spectra did not exceed 45 seconds and precautions were taken to ensure constancy of temperature during this interval. To obtain the extinction coefficient, the Bunsen-Roscoe formula was employed and readings were taken on the "Density-Scale" of the rotating circle. Thus the extinction coefficient is given by $\Sigma = \frac{D}{t}$ where "D" is the reading on the density scale and equal to $2\log_{10}\tan\theta$, "θ" being the angular reading and t the thickness in centimeters of the absorbing substance.

Experimental.

1. Molybdic acid was prepared by adding equivalent amount of HCl to 2% ammonium molybdate solution.

TABLE I.

15 C.c. molybdic acid sol + 0·3 c.c. absolute alcohol.

Temperature = 26·5°.

Condition.	Time in min.	Extinction coefficient.	k_0 Zero-molecular.
Fresh sample	12	0·56	—
	24	0·90	0·0284
	36	1·26	0·0290
	48	1·65	0·0300
			Mean 0·0291
Old sample	8	0·44	—
	20	0·76	0·0267
	32	1·06	0·0258
	44	1·36	0·0255
			Mean 0·0260
Old sample heated to 70° for 8 minutes.	4	0·20	—
	16	0·62	0·035
	28	1·04	0·035
	40	1·46	0·035
			Mean 0·035

TABLE II.

10 C.c. molybdic acid + 3 c.c. water + 2 c.c. water or electrolyte + 0·3 c.c. absolute alcohol.

Condition.	Time in min.	Extinction coefficient.	k_0 Zero-molecular.
2 c.c. water	5	0·02	—
	20	0·32	0·020
	35	0·61	0·0196
	50	0·92	0·020
			Mean 0·0199
2 c.c. *N*/10-NaCl	10	0·08	—
	25	0·34	0·0173
	40	0·58	0·0167
	55	0·81	0·0163
			Mean 0·0166
2 c.c. *N*/10-KCl	6	0·05	—
	15	0·16	0·0120
	24	0·26	0·0117
	33	0·35	0·0112
			Mean 0·0116
2 c.c. *N*/10-RbCl	15	0·28	—
	30	0·38	0·0067
	45	0·50	0·0078
	60	0·59	0·0069
			Mean 0·00697
2 c.c. *N*/10-LiCl	9	0·12	—
	18	0·29	0·0190
	27	0·45	0·0180
	36	0·60	0·0177
			Mean 0·0182

2. Tungstic acid was prepared by adding equivalent amount of HCl to $M/10$-sodium tungstate solution.

TABLE III.

10 C.c. tungstic acid + 0·5 c.c. alcohol + 4·5 c.c. water or electrolyte.

Temperature = 15 c.c. Total volume = 25°.

Condition.	Time in min.	Extinction coefficient	k_0 Zero molecular.
4·5 c.c. water.	3	0·06	—
	15	0·20	0·0117
	27	0·34	0·0116
	39	0·48	0·0116
			Mean 0·0116
2N-LiCl	6	0·12	—
	18	0·24	0·0100
	30	0·36	0·0100
	42	0·47	0·0097
			Mean 0·0099
2N-NaCl	9	0·14	—
	21	0·25	0·0091
	33	0·35	0·0087
	45	0·46	0·0089
			Mean 0·0089
2N-KCl	12	0·17	—
	24	0·26	0·0075
	36	0·36	0·0079
	48	0·45	0·0077
			Mean 0·0077

The photochemical reduction of the sols of molybdic and tungstic acids by ethyl alcohol thus follows the zero-molecular law. On the other hand, Wassiljewa found that the reduction follows the monomolecular law. Reduction cannot be observed in the dark. Dhar (*J. Chem. Soc.*, 1923, **123**, 1856) has shown that the order of a photochemical reaction is generally decreased in the presence of light and this decrease is most remarkable in the chemical reactions which are highly photosensitive such as the present ones.

It may be interesting to note that the velocity constant of freshly prepared molybdic acid sol decreases from 0·0291 to 0·0260 when it is allowed to age for two days. When, however, the sol is heated to 70° for about 8 minutes the velocity constant is increased

to 0·035 and it is greater than the velocity constant of the freshly prepared sol. We have already shown in a separate paper (*loc. cit.*) that molybdic acid gradually polymerises to bigger molecules on ageing and when the sol is heated, the aggregated molecules again broken up into simple molecules.

The sols become less photochemically active in the presence of monovalent cations, and the velocity constants are smaller than that of the fresh sol. The order in which the cations affect the velocity constants are in the order Rb $>$ K $>$ Na $>$ Li, Rb decreasing the velocity constant to the greatest extent and Li the least.

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Reversal of Charge of Serum and its Coagulation and Gelatinisation with Acids.

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In a previous communication (*J. Indian Chem. Soc.*, 1928, **5**, 313) the authors have shown that polyvalent cations and acids possess high coagulating powers towards serum and that dilution stabilises serum against coagulation by univalent ions derived from salts like sodium acetate, potassium fluoride, oxalate, etc. While the normal dilution effect has been observed when serum is coagulated by acids and polyvalent cations, marked ionic antagonism is developed when it is coagulated by the cations of varying valencies or an acid and a salt. The phenomenon of positive acclimatisation is more marked for the diluted serum than the concentrated one when coagulated by salts, while with acids, the phenomenon is less developed with dilute serum. We have shown that like the sols of gamboge, mastic, arsenious sulphide, etc., serum is also capable of adsorbing similarly charged ions when coagulated with electrolytes.

In the present investigation, we have found that there are two distinct points of coagulation for serum, one with dilute and the other with concentrated acids. The gelatinisation of serum by acids has also been studied.

Goat blood was collected in a glass vessel in which it clotted within a few minutes. The clear straw-coloured serum which was squeezed out due to syneresis was used.

Two c. c. of original serum were made up to 10 c. c. with different concentrations of dilute or concentrated acid and the requisite amount of water; the coagulation was observed after one hour.

Table I.

Concentrations in normality of dilute and concentrated acids are shown in coloumns I and II respectively.

Acids.	I	II	Acids.	I	II
HCl	0·0029	0·1275	Cl_3COOH	0·0034	0·0348
HNO_3	0·0034	0·0889	HCOOH	0·0036	5·9454
H_2SO_4	0·0024	0·1161	CH_3COOH	0·0038	2·8458
$CH_2ClCOOH$	0·0024	0·6854	H_3PO_4	0·0033	0·6304

The effect of dilution of serum on coagulation with concentrated acids has also been investigated.

A/2 serum=1 c. c. of serum. A serum=2 c. c. of serum. 2A serum=4 c.c. of serum. Total volume=10 c. c. Time=1 hour.

TABLE II.

Acids.	Volume in c. c. necessary for coagulation.		
	A/2	A	2A
1·75*N*-HCl	1·6	1·3	1·0
0·741*N*-HNO_3	1·5	1·2	0·8
1·452*N*-H_2SO_4	1·4	0·8	0·55
4·896*N*-$CH_2ClCOOH$	2·3	1·4	0·6
0·174*N*-CCl_3COOH	2·4	2·0	1·4
22·02*N*-HCOOH	3·6	2·7	1·3
15·81*N*-CH_3COOH	3·2	1·8	1·0
7·88*N*-H_3PO_4	1·3	0·8	0·45

From the results recorded above, it will be seen that for the second point of coagulation, much higher concentrations of acids are necessary than for the first point; and when the serum is coagulated by concentrated acids, it behaves abnormally towards dilution, due to its marked tendency of adsorbing similarly charged ions from the acids. It has been found (*loc. cit.*) that for the first point of coagulation by dilute acids, the serum behaves normally towards dilution, and smaller amounts of acids are necessary to coagulate the dilute serum than the concentrated one.

Serum is not coagulated even by molar solutions of ammonium sulphate; its globulin content is only precipitated out when it is half saturated with the salt. The results recorded in the following table show that in presence of small quantities of acids, serum is sensitised and is easily coagulated by ammonium sulphate. When the amount of hydrochloric acid added to the serum is small, the serum becomes unstable towards ammonium sulphate. This behaviour has been explained on the assumption that in presence of small amounts of acid, the hydrolysis of serum is checked and thus it is made unstable. Similar results have been obtained with the sols of Prussian blue, copper ferrocyanide, arsenious sulphide, gamboge, mastic and gum dammar (compare *J. Phys. Chem.*, 1926, **30**, 830; *Kolloid Z.*, 1926, **29**, 346).

TABLE III.

Amount of serum = 2 c. c. Total volume = 10 c. c. Time = 1 hour.

Volume in c. c. of 1·75*N*-Hydrochloric acid added.	Volume c. c. of *M*/10-Ammonium sulphate necessary for coagulation.
1·3	0
0	more than 5 c. c. of 2*M*
0·2	0·8
0·3	1·7
0·4	2·6
0·5	1·6

From these results, it appears that as the concentration of hydrochloric acid is increased, the serum becomes more and more stabilised by the adsorption of hydrogen ions, and evidently there is a reversal of the charge on the serum, which becomes positive on account of the adsorption of hydrogen ions. With higher concentrations of acids, both cations and anions influence the coagulation points, and the positively charged serum is coagulated by anions. The marked tendency of adsorbing similarly charged hydrogen ions by the positively reversed serum is shown from the fact that dilute serum is more stable towards coagulation by concentrated acids than concentrated serum.

Serum contains, besides other substances, two proteins, *viz.*, serum albumin and serum globulin, and it has long been known that serum globulin is precipitated when it is half saturated with ammonium sulphate, but serum albumin is only obtained when the filtrate after removing globulins is saturated with ammonium sulphate and acidified with 10% acetic acid (resulting solution containing 1% acetic acid) and allowed to stand for two hours or longer. The addition of acetic acid for the precipitation of albumin by ammonium sulphate is in accord with the view just stated and it appears that on the addition of sufficient quantity of acids, a reversal in the charge of serum takes place, which helps its coagulation by multivalent anions.

It appears that in these coagulation experiments on serum, the whole of the colloidal phase is never completely precipitated. When serum is coagulated by dilute acids or by sodium acetate, tartrate, citrate, etc., it is mainly the globulin portion which is thrown down as is the case when it is half saturated with ammonium sulphate. But serum albumin is also precipitated when coagulation is carried by either concentrated acids or salts with polyvalent cations. Two distinct points of coagulation as with acids are also obtained when serum is coagulated by such electrolytes as aluminium nitrate, cerous nitrate, thorium nitrate, copper sulphate, etc.

The coagulation of serum by acids appears to be mainly controlled by hydrogen-ion concentrations. In the following table, we are recording the variation in p_H values with different amounts of acids, p_H values were determined by indicator method, using nitrophenols as indicators. Original serum had a $p_H = 7{\cdot}8$. On diluting serum with water, an opalescent solution is obtained and on the addition of dilute acids, turbidity at first increases corresponding to the first coagulation point, but after a certain concentration, the solution begins to clear indicating the beginning of the reversal of charge and on further addition of the electrolytes, quite transparent serum is obtained when the charge reversal is complete.

Original serum $\rightarrow p_H = 7{\cdot}8$.
2 C. c. of serum + 8 c. c. water $\rightarrow p_H = 7{\cdot}6$.

2 C. c. of serum were mixed with different concentrations of N-10 acids and the total volume was made up to 10 c. c. The hydrogen-ion concentrations are recorded in the following table.

TABLE IV.

Volume. in c c. of N/10 acid.	Hydro. cloric acid.	Nitric acid.	Sulphuric acid.	Mono chlor-acetic acid.	Tri chlor-acetic acid.	Formic acid.
	p_H	p_H	p_H	p_H	p_H	p_H
0·1	7·3	7·3	7·3	7·5	7·5	7·3
0·3	6·8A	6·9A	7·0A	7·15A	6·9A	6·9A
0·5	6·0	6·2	6·3	6·6	6·2	6·4
0·6	—	—	6·1	—	—	—
0·7	5·6B	5·6B	6·7	6·1	5·7	6·0
0·9	—	—	5·6	—	—	—
1·0	5·4	5·5	5·4	5·4	5·3	5·4
1·1	5·3	—	—	—	4·9B	—
1·2	5·2C	5·3C	5·3B	5·3B	4·7	5·3B
1·4	—	4·9	4·9	5·2	4·4C	5·3
1·5	4·9	—	—	—	—	—
1·6	—	—	4·6	5·0C	4·4	5·3
1·8	—	—	4·3C	4·7	—	5·3C
2·0	—	—	4·0	—	—	5·1

From A to B—Region of first coagulation point.
At B—Opalescence begins to disappear and reversal of charge begins.
At C—Reversal of charge is complete.

From the above table it will be seen that the charge reversal takes place in almost the same region for different acids.

TABLE V.

Acids.	Charge reversal region.	Acids.	Charge reversal region.
HCl	*p*H 5·5—5·3	$CH_2ClCOOH$	*p*H 5·3—5·0
HNO_3	5·6—5·3	CCl_3COOH	4·9—4·4
H_2SO_4	5·3—4·3	HCOOH	5·3

From this it will be seen that the conditions most favorable for the charge reversal of serum are near the *p*H 5·3—5·0. As has already been stated that the dissolution of the turbid phase was taken as an indication of the reversal of charge, some allowance has to be made in the measurements where the anion effects are more marked as in the case of sulphuric acid, where due to the coagulating influence of SO_4'' ions on the positively charged serum, the turbidity did not disappear till it had reached the *p*H 4·3. Thus it appears that the coagulation of serum by dilute acids is mainly a function of hydrogen-ion concentrations, and anions exert only a secondary influence.

The coagutating power of concentrated acids for the second point as seen from Table I is in the following order:—

Trichloracetic> nitric> sulphuric> hydrochloric> hypophosphorous> monochloracetic> acetic> formic. From this it appears that the degree of dissociation of the acids influence the coagulation of serum markedly so far as the second coagulation point is concerned.

The two coagulation points of serum also affect the hydration tendency of particles differently in the two cases. From the nature of the coagulated mass it appears that serum coagulated by dilute acids is more flocculent than gelatinous. After the reversal of charge, further coagulation is accompanied by marked adsorption of the solvent medium, and the viscosity of the system also gradually increases, and finally under suitable concentrations, stable jellies of the serum are obtained. It appears that serum albumin which has a greater probability of being precipitated near the second coagulation point, is more liable of hydration than the serum globulin which is exclusively precipitated by dilute acids.

In the following tables, observations on gelatinisation of serum by different acids are recorded. A certain volume of serum mixed and well-shaken with different amounts of acids was made up to 5 c.c. in every case with the requisite amount of water and the time of setting to jellies was noted.

TABLE VI.

Gelatinisation by Hydrocloric Acid.

3 G.c. of serum mixed with varying amounts of HCl and the total volume made up to 5 c.c.

1·75*N*-HCl.	Observation.	1·75*N*-HCl.	Observation.
1·0 c.c.	No jelly in 2 days.	1·6 c.c.	Opaque jelly in 22 hrs.
1·2	No jelly in 2 days.	1·8	Opaque jelly in 3 hrs.
1·4	Opaque jelly in 22 hrs.	2·0	Flocculent precipitate, setting to loose jelly within 22 hrs.

TABLE VII.

Gelatinisation by Nitric, Sulphuric and Trichloracetic Acids.

Serum can also be gelatinised by other strong acids, such as nitric, sulphuric, and trichloracetic, like hydrochloric acid, and the jellies thus obtained are mostly opaque.

Total volume = 5 c.c.

Vol. of serum (c.c.).	Volume of acids (c.c.)			
	2·965*N*-HNO_3.	7·26*N*-H_2SO_4.	0·879*N*-CCl_3COOH.	Time of gelation.
3	0·1—0·3	—	0·1—0·3	No jelly.
	—	0·8	—	Jelly within 1 day.
	0·4	1·1—1·4	0·4	Within 3 to 7 hours.
	0·6	—	0·5—0·6	Within 10 minutes.
4	0·2	—	0·3—0·4	No jelly.
	—	0·4—0·6	—	Jelly in 1 day.
	—	0·8—1·0	—	Within 4 to 6 hours.
	0·3—0·4	—	0·5	Within 1 to 4 hours.
	0·5	—	0·6	Within ½ hour.
4·5	—	—	0·4—0·5	No jelly.
	0·2	0·2—0·5	—	Jelly within 1 day.
	0·3	—	—	Within 3½ hours.
	0·4	—	—	Within 25 minutes.

TABLE VIII.

Gelatinisation by Acetic Acid.

Total Vol. = 5 c.c.

Vol. of serum.	Vol. of 15·81 *N*-acetic acid (glacial).	Observation.
3 c.c.	0·5 c.c.	No jelly in 1 day.
3	1·0	Translucent jelly in 40 mins.
3	1·5	Opaque jelly in 3 mins.
3	2·0	Opaque jelly in 2 mins.
4	0·1	No jelly in 1 day.
4	0·4	Translucent jelly in 3 days.
4	0·7	Translucent jelly in 45 mins.
4	1·0	Translucent jelly in 3 mins.
4·5	0·1	No jelly in 1 day.
4·5	0·3	No jelly in 1 day.
4·5	0·5	Translucent jelly in 1 day.

TABLE IX.

Gelatinisation by Monochloracetic Acid.

Total vol. = 5 c.c.

Vol. of serum (c.c.).	Vol. of 4·896-*N*. $CH_2ClCOOH$. (c.c.).	Observation.
3	0·3	No jelly.
3	0·6	Translucent jelly in 1 day.
3	0·9	Translucent jelly in 1 hr.
3	1·2	Opaque jelly in 25 mins.
4	0·4	Translucent jelly in 1 day.
4	0·6	Translucent jelly in 2½ hrs.
4	0·8	Translucent jelly in 25 mins.
4	1·0	Loose translucent jelly in 1 day.
4·5	0·3	Translucent jelly in 1 day.
4·5	0·4	Translucent jelly in 1 day.
4·5	0·5	Translucent jelly in 3 hrs.

TABLE X.

Gelatinisation by Formic Acid.

Total vol. = 5 c.c.

Vol. of serum (c.c.).	Vol. of 22·02 *N*-formic acid (c.c.).	Observation.
3	0·4	No jelly in 1 day.
3	0·6	No jelly in 1 day.
3	0·8	Translucent jelly in 1 day.
4	0·4	No jelly in 1 day.
4	0·6	Translucent jelly in 3½ hrs.
4	0·8	Translucent jelly in 20 mins.
4	1·0	Translucent jelly in 3 mins.
4·5	0·1	No jelly in 1 day.
4·5	0·3	No jelly in 1 day.
4·5	0·5	Translucent jelly in 2½ hrs.

TABLE XI

Gelatinisation by Oxalic Acid.

No jelly could be obtained by using even saturated solution of oxalic acid. However, jellies could be prepared by shaking serum with solid oxalic acids and allowing it to set.

Total vol. = 5 c.c.

Vol. of serum (c.c.).	Amount of solid oxalic acid (g.).	Observation.
3	0·9	No jelly even in 3 days.
3	1·1	No jelly even in 3 days.
3	1·3	Translucent jelly in 3 days.
4	0·7	Loose translucent jelly in 1 day.
4	0·9	Loose translucent jelly in 1 day.
4	1·1	Firm translucent jelly in 1 day.
4	1·3	Firm translucent jelly in 1 day.
4·5	0·5	Opaque jelly in 1 day.
4·5	0·7	Opaque jelly in 1 day.
4·5	0·9	Opaque loose jelly in 1 day.

TABLE XII.

Gelatinisation by Hypophosphorous Acid.

Total vol. = 5 c.c.

Vol. of serum (c.c.).	Vol. of 7·888 *N*-hypophosphorous acid (c.c.).	Observation.
3	0·5	No jelly in 1 day.
3	0·8	No jelly in 1 day.
3	1·1	Translucent jelly in 1 day.
3	1·4	Opaque jelly in 1 day.
4	0·4	No jelly in 1 day.
4	0·6	No jelly in 1 day.
4	0·8	Translucent jelly in 1 day.
4	1·0	Translucent jelly in 4½ hrs.
4·5	0·3	No jelly in 1 day.
4·5	0·4	No jelly in 1 day.
4·5	0·5	Translucent jelly in 1 day.

TABLE XIII.

Gelatinisation by Aluminium Nitrate.

Total vol. = 5 c.c.

Vol. of serum (c.c.).	Vol. of $M/1{\cdot}27$-aluminium nitrate (c.c.).	Observation.
3	0·5	No jelly.
3	1·0	Opaque jelly in 1 day.
3	1·5	Opaque jelly in 1 hr.
3	2·0	Opaque loose jelly immediately.
4	0·8	No jelly.
4	1·0	Opaque jelly in 1 day.
4·5	0·3	Opaque jelly in 1 day.

It will be seen from these tables that the jellies of the best texture are obtained by using weak acids. Glacial acetic, formic, monochloracetic, hypophosphorous and oxalic acids yield almost transparent jellies, while strong acids such as hydrochloric, sulphuric nitric and trichloracetic acids yield opaque jellies. Salts containing polyvalent cations, like aluminium nitrate also give opaque jellies. These jellies are very stable; they do not undergo any marked syneresis, though putrefaction begins after a couple of days. An attempt to gelatinise serum by very weak acids like citric, tartaric and phosphoric acids has been so far unsuccessful. It appears that it is partly due to the weak nature of these acids and partly due to the fact that their solutions cannot be obtained in such concentrations as those of formic and acetic acids. The gelatinisation of serum appears to be a function of hydrogen ion concentration. The concentrations of the acids used for this purpose are in the following order:—

Trichloracetic<nitric<sulphuric<hydrochloric<monochloracetic <hypophosphorous<acetic<formic.

This order generally agrees with that of concentrated acids, in similar experiments.

We have already shown that serum behaves abnormally towards dilution when coagulated by concentrated acids. Our results on gelatinisation of serum, also show that with increased concentration of serum, the amount of acid required to produce a jelley in a definite time decreases, that is, much less acid is required to produce a jelly with concentrated serum than with dilute one.

Summary.

1. It has been observed that there are two distinct points of coagulation, when serum is coagulated by acids or salts of polyvalent cations. The first point is obtained by using zilute acids, and the second by concentrated acids.

2. The coagulating power of concentrated acids for the second point is in the following order: –

Trichloracetic>nitric>sulphuric>hydrochloric>hypophosphorous >monochloracetic>acetic>formic.

3. When serum is coagulated by concentrated acids, it behaves abnormally towards dilution, as it has a high tendency of absorbing similarly charged ions from the acids.

4. It has been shown that in the presence of small quantities of acids, serum is sensitised, and is easily coagulated by ammonium sulphate. This is partly due to the fact that the hydrolysis of serum is checked by acids and partly because the charge on serum is reversed by the adsorption of hydrogen ions.

5. It has been shown that charge reversal of serum takes place near p_4 5·3-5·0, when serum is coagulated by acids. It is the globulin portion of serum which is exclusively precipitated by dilute acids near the first coagulation point, while at the second coagulation point, serum albumin is also thrown down.

6. When serum is coagulated by dilute acids, the precipitated mass is flocculent, while with concentrated acids, a gelatinous mass is obtained. Under suitable concentrations of acids, jellies of serum can also be obtained.

7. Very stable translucent jellies of serum undergoing no marked syneresis are obtained when serum is coagulated by concentrated solutions of acetic, monochloracetic, formic and hypophosphorous acids and solid oxalic acid. Hydrochloric, nitric, sulphuric and trichloracetic acids yield opaque stable jellies of serum.

8. The concentrations of acids necessary for the preparation of jellies are in the following order:—

Trichloracetic<nitric<sulphuric<hydrochloric<monochloracetic <hypophosphorous<acetic<formic.

9. As the concentration of serum increases, the amount of acid required to gelatinise serum in a definite time decreases.

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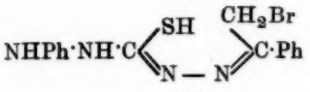
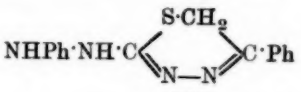
Thiodiazines. Part VI.

By Prafulla Kumar Bose and Birendra Kumar Nandi.

While studying the action of phenylthiocarbohydrazide upon ω-bromoacetophenone, Guha and Ray-Choudhury (*J. Indian Chem. Soc.*, 1928, **5**, 153) made the assumption that the -CO- group of the bromo-ketone first acted on the hydrazino-residue of the hydrazide leading to the formation of the intermediate compound (I, type *a*),



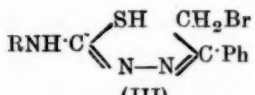
(I)



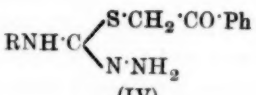
(II)

which finally lost hydrogen bromide to give the thiodiazine (II). The mechanism proposed above by Guha and Ray-Choudhury is different from what one of us suggested (Bose, *J. Indian Chem. Soc.*, 1924, **1**, 51) and consequently it was deemed necessary to study the subject further.

The isolation of a compound (III, type *a*) or (IV, type *b*) from the product of interaction of ω-bromoacetophenone and a thiosemicarbazide would have definitely settled this point. But this was unsuccessful (Part I). It has however been pointed out in Part I as well as in Part II of this series (Bose, *J. Indian Chem.Soc.*, 1925, **2**, 100) that varying quantities of thiazoles are formed in the thiodiazine condensation referred to above.



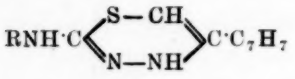
(III)



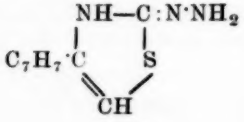
(IV)

The formation of these can be very easily explained by assuming an intermediate compound of the type (*b*) *i.e.*, (IV). A compound of the type (*a*) can never give rise to a thiazole derivative directly by elimination of hydrobromic acid.

Further evidences as to the nature of the intermediates were sought to be gathered from the interaction between a thiosemicarbazide and *p*-methyl-ω-bromo-acetophenone. But unfortunately the results obtained, even under varied conditions, were inconclusive. This reaction was found to lead either to a thiodiazine or to a thiazole and not to both, which is remarkable in view of our previous experiences. Thiodiazines (V) are obtained by using 4-substituted thiosemicarbazides. The constitution of the products was indirectly ascertained by observing the absence of reactivity towards aldehydes and ketones.

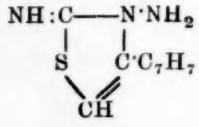


(V)

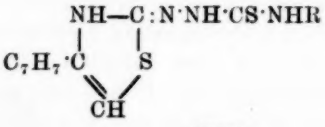


(VI)

A thiodiazole (VI) is obtained using thiosemicarbazide. The constitutional formula of this compound was established by converting it into the monoacetyl and benzylidene derivatives and proving their identity with the corresponding products synthesised from acetyl- and benzylidene-thiosemicarbazides. Any claims to the alternative thiazole formula (VII) for the substance are thus rejected.

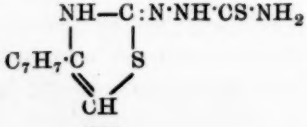


(VII)

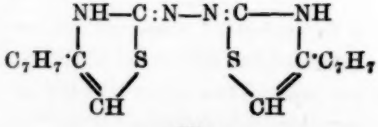


(VIII)

The compound (VI) also reacted with *iso*thiocyanates and thiocyanic acid producing additive compounds of the type (VIII) and (IX) respectively. The latter again could be condensed with a further molecule of *p*-methyl-ω-bromo-acetophenone yielding (X). This was prepared in connexion with another investigation.



(IX)



(X)

Experimental.

2-*Keto*-4-p-*tolyl*-2:3-*dihydro*-1:3-*thiazolehydrazone* (VI).

Thiosemicarbazide (one mol., 1 g.) and *p*-methyl-ω-bromoacetophenone (1 mol., 2·3 g.) were shaken with 35 c.c. of absolute alcohol. The reactants gradually passed into solution with development of heat. After a few minutes a precipitate separated out. To ensure the completion of the reaction the whole thing was heated on a water-bath under reflux for 15-20 minutes. The mixture was cooled and diluted with ether. The crude crystalline hydrobromide of the base (2·4 g.) was collected, washed thoroughly with ether and dried on a porous plate.

To obtain the free base, the hydrobromide was dissolved in boiling dilute hydrochloric acid when most of the solid went into solution. A little tarry matter and some solid remained undissolved. These were filtered off while hot and the filtrate was neutralised with a dilute solution of sodium carbonate when the solution turned milky, and shortly afterwards needle-shaped crystals appeared. These were collected, redissolved in hot dilute hydrochloric acid, filtered, and again precipitated with sodium carbonate solution (yield, 1·2 g.). When crystallised form methyl alcohol in colourless needles, it melted at 178°. (Found: C, 58·39; H, 5·28; N, 20·55. $C_{10}H_{11}N_3S$ requires C, 58·54; H, 5·37; N, 20·49 per cent.).

The base is soluble in ethyl alcohol, benzene and pyridine but crystallises best from methyl alcohol. On exposure to air it gradually turns brown owing to atmospheric oxidation.

The *hydrochloride* was obtained by dissolving the base in boiling hydrochloric acid (20%) and allowing the solution to cool. It was recrystallised from alcohol in colourless plates, m.p. 133°. (Found: N, 17·21. $C_{10}H_{12}N_3SCl$ requires N, 17·39 per cent.).

The *benzylidene derivative of* (VI) crystallised in colourless needles from absolute alcohol. It is soluble in pyridine and acetone but sparingly so in benzene; m.p. 205°. (Found: N, 14·46. $C_{17}H_{15}N_3S$ requires N, 14·34 per cent.).

Benzylidenethiosemicarbazone and p-*Methyl*-ω-*bromoacetophenone.*—The condensation was effected in alcoholic medium as described above using molecular proportions. The free base was precipitated from the solution by adding a little pyridine and water, and was finally crystallised from alcohol. The m.p. of this base alone or when mixed with the above product was found to be 205°.

2-Keto-4-p-tolyl-2 : 3-dihydro-1 : 3-thiazole-isopropylidenehydrazone was obtained by heating the base with acetone under reflux for about half an hour. On dilution with water a precipitate was formed which was crystallised from alcohol in very pale yellow crystals melting at 230°. (Found: N, 17·22. $C_{13}H_{15}N_3S$ requires N, 17·14 per cent.).

The *benzoyl* derivative crystallised in needle-shaped colourless crystals form alcohol, m.p. 201°. (Found: N, 13·71. $C_{17}H_{15}ON_3S$ requires N, 13·58 per cent.).

The *acetyl derivative* of (VI) was prepared by heating the base, 2-keto-4-*p*-tolyl-2 : 3-dihydro-1 : 3-thiazolehydrazone, with acetic anhydride and a little pyridine for about 25 minutes. It separated in colourless, long needles from methyl alcohol, m.p. 195°. (Found: N, 17·03. $C_{12}H_{13}ON_3S$ requires N, 17·00 per cent.). It is soluble in alcohol and benzene. The compound is very stable and does not, like the free base, change colour when exposed to the atmosphere.

Condensation of 1-Acetylthiosemicarbazide and Methyl-ω-bromo-p-acetophenone.—The condensation product was obtained by heating acetylthiosemicarbazide (2 g.) and *p*-methyl-ω-bromoacetophenone (2·3 g.) in alcohol (30 c.c.) for a few minutes. The substance crystallised from absolute alcohol in colourless, long needles, m.p. 195°. It dissolved in warm alkali and was found to be identical with the acetyl derivative described above.

2-Keto-4-p-tolyl-2 : 3-dihydro-1 : 3-thiazolethiosemicarbazone (IX). ——To 100 c.c. of dry absolute alcohol containing 0·9 g. of dry hydrochloric acid gas, 5 g. of the base (VI) and 3 g. (excess) of potassium sulphocyanide were added and the mixture was refluxed on a water-bath for 6—7 hours. The potassium chloride obtained on cooling the reaction mixture was filtered off and the filtrate, on concentration, deposited crystals which were recrystallised in beautiful glistening plates (pinkish) from absolute alcohol. It melts at 218° and is soluble in most organic media. (Found: N, 21·37. $C_{11}H_{12}N_4S$ requires N, 21·27 per cent.).

2-Keto-4-p-tolyl-2 : 3-dihydrothiazolethiosemicarbazone and p-Methyl-ω-bromoacetophenone: Formation of (X).—The thiosemicarbazone (0·5 g.) dissolved is absolute alcohol (10 c.c.) was thoroughly shaken with *p*-methyl-ω-bromoacetophenone (0·4 g.) for some time at the ordinary temperature and finally heated under reflux on a water-bath for a few minutes. The condensation product which separated

was collected. For purification it was extracted with hot dilute hydrochloric acid, and the extract made alkaline with a dilute solution of sodium carbonate when the product crystallised out. This was recrystallised from alcohol in colourless needles, m. p. 120°. (Found: N, 14·39. $C_{20}H_{18}N_4S_2$ requires N, 14·82 per cent).

2-Keto-4-p-tolyl-2 : 3-dihydro-1 : 3-thiazole-4-methylthiosemicarbazone (VIII, R=CH_3).—To an alcoholic solution of compound (VI) methyl *iso*thiocyanate was added drop by drop. On slight warming and then cooling a precipitate appeared. This was crystallised from methyl alcohol in yellowish needles, m.p. 146°. (Found: N, 19·93. $C_{12}H_{14}N_4S_2$ requires N, 20·14 per cent.).

Similar additive products were obtained with phenyl-, *o*-tolyl- and *p*-tolyl-*iso*thiocyanates. The *phenyl* derivative (from alcohol) had m.p. 191°. (Found: N, 16·39. $C_{17}H_{16}N_4S_2$ requires N, 16·47 per cent.).

The o-*tolyl*-derivative formed slightly pink needles from alcohol, m.p. 174°, soluble in alcohol, ether, benzene and acetone. (Found: N, 16·10. $C_{18}H_{18}N_4S_2$ requires N, 15·82 per cent.).

The p-*tolyl*-derivative was a pale yellow crystalline substance (from alcohol), m.p. 166°. (Found: N, 15·88. $C_{18}H_{18}N_4S_2$ requires N, 15·82 per cent.)

2-Methylamino-5-p-tolyl-1 : 3 : 4-thiodiazine (V, R=CH_3).—To 4-methylthiosemicarbazide (2 g.) dissolved in 30 c.c. of absolute alcohol, *p*-methyl-ω-bromoacetophenone (4·1 g.) was added. The reaction was completed by heating under reflux for 15 minutes. The hydrobromide of the base separated in yellow clusters. These were filtered off and the free base separated as described before.

The base crystallised in colourless needles from alcohol and melted at 249°. It is soluble in alcohol, pyridine and benzene, but insoluble in ether. (Found: N, 19·00. $C_{11}H_{13}N_3S$ requires N, 19·17 per cent.).

The *hydrochloride* of the base crystallised from dilute alcohol (60 per cent.) in colourless plates, m.p. 195°. (Found: N, 16·20. $C_{11}H_{14}N_3SCl$ requires N, 16·07 per cent.).

*4-iso**Butylthiosemicarbazide*, $C_4H_9NH{\cdot}CS{\cdot}NH{\cdot}NH_2$.—Hydrazine hydrate (5 g.) was dissolved in 20 c.c. of absolute alcohol and the solution cooled in ice. *iso*Butyl*iso*thiocyanate (11·5 g.) was then dropped into the cooled solution with frequent shaking. After a few minutes colourless, silky, glistening crystals appeared. These were filtered off and washed with 10 per cent. alcohol. It

crystallised in beautiful long needles from rectified spirit. It is very soluble in alcohol ; m.p. 79° (yield almost quantitative.). (Found: N, 28·50. $C_5H_{13}N_3S$ requires N, 28·57 per cent.).

The *benzylidene* derivative, $C_4H_9NH{\cdot}CS{\cdot}NH{\cdot}N{:}CHPh$, which was easily prepared in alcoholic medium, formed colourless silky needles, m.p. 125°.

The iso*propylidene* derivative, $C_4H_9NH{\cdot}CS{\cdot}NH{\cdot}N{:}CMe_2$ was prepared by boiling the substance with acetone for a few minutes. It formed silky plates, m.p. 112°.

2-iso*Butylamino*-5-p-*tolyl*-1:3:4-*thiodiazine* (V, R=*iso*butyl).—4-*iso*Butylthiosemicarbazide (3 g.) dissoved in 30 c.c. of absolute alcohol was treated with *p*-methyl-ω-bromoacetophenone (4·4 g.): the mixture was shaken, and finally heated on a water-bath for 25 minutes. On cooling, yellow clusters appeared which increased on the addition of ether to the solution. The hydrobromide was collected, and the base liberated as usual by dilute sodium carbonate. The crude brownish precipitate was crystallised from alcohol (charcoal) in colourless needles, m.p. 159°. It is soluble in benzene, pyridine and acetone. (Found: C, 64·15; H, 7·35; N, 16·00. $C_{14}H_{19}N_3S$ requires C, 64·36; H, 7·27; N, 16·09 per cent.). The base turns brown on standing in air, especially when moist.

The *hydrochloride* crystallised in colourless leaflets from alcohol having m.p. 125°. (Found: N, 14·18. $C_{14}H_{20}N_3SCl$ requires N, 14·11 per cent.).

The *acetyl* derivative, prepared in the usual maner, crystallised from alcohol in light yellow crystals, m.p. 167°. (Found: N, 13·78. $C_{16}H_{21}ON_3S$ requires N, 13·86 per cent.).

2-*Phenylamino*-5-p-*tolyl*-1:3:4-*thiodiazine* (V, R=Ph).—From 3 g. 4-phenylthiosemicarbazide in 50 c.c. of absolute alcohol and 3·8 g. *p*-methyl-ω-bromoacetophenone, 1·8 g. of the purified base were obtained. It crystallised from alcohol in colourless needles after treatment with charcoal; m.p. 198°. (Found: N, 15·01. $C_{16}H_{15}N_3S$ requires N, 14·94 per cent.).

The *hydrochloride* separated from dilute alcohol in colourless plates, m.p. 135°. (Found: N, 13·41. $C_{15}H_{16}N_3SCl$ requires N, 13·22 per cent.).

The *acetyl* derivative crystallised from absolute alcohol melted at 170°. (Found: N, 13·19. $C_{18}H_{17}ON_3S$ requires N, 13·00 per cent.).

2-o-*Tolylamino*-5-p-*tolyl*-1:3:4-*thiodiazine* (V, R=*o*-tolyl).—It was prepared in a similar way. The free base was obtained in needles, having a slight brownish tint, m.p. 179°. (Found: N, 14·14. $C_{17}H_{17}N_3S$ requires N, 14·24 per cent.).

The *hydrochloride* separated in colourless crystals from dilute alcohol, m.p. 171°. (Found: N, 12·43. $C_{17}H_{18}N_3SCl$ requires N, 12·66 per cent.)

The *acetyl* derivative crystallised in colourless needles from absolute alcohol in which it was moderately soluble. It melts at 199°. (Found: N, 12·40. $C_{19}H_{19}ON_3S$ requires N, 12·46 per cent.).

2-p-*Tolylamino*-5-p-*tolyl*-1:3:4-*thiodiazine* (V, R=*p*-tolyl) was obtained in the usual manner from 4-*p*-tolylthiosemicarbazide and *p*-methyl-ω-bromoacetophenone. It formed almost colourless prisms, m.p. 187°, from a mixture of ethyl and methyl alcohol (1:1). It is also soluble in pyridine and benzene. (Found: N, 14·29. $C_{17}H_{17}N_3S$ requires N, 14·24 per cent.).

The *hydrochloride* was obtained by treating the base with dilute hydrochloric acid and crystallising the product from alcohol, m p. 199°.

The *acetyl* derivative was obtained in prisms from alcohol; m.p. 154°. (Found: N, 12·50. $C_{19}H_{19}ON_3S$ requires N, 12·46 per cent.)

Our best thanks are due to Sir P. C. Rây for his kind interest in this investigation.

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and Technology, Calcutta.

Received February 22, 1930.

A Note on the Magnetic Susceptibility of certain Complex Molybdenum Compounds.

By Priyada Ranjan Rây.

In a previous paper to this journal (Rây and Bhar, 1928, **5**, 497) it was shown that two of the complex molybdenum compounds examined behaved like the corresponding chromium complexes regarding their magnetic properties. The compounds studied were K_3MoCl_6, $2H_2O$ and $(NH_4)_3Mo(SCN)_6, 4H_2O$. Both were found to obey Bose's rule giving a Bohr-magneton value of three each. This is evident from the effective atomic-numbers for the central molybdenum atom in them. The number in these cases is equal to $(42-3+12)=51$, three units less than the atomic number for the nearest inert gas xenon (54). The valency of the molybdenum atom in these two compounds is three, corresponding to that of chromium in chromic complexes. On the other hand it was also found that (*loc. cit.*) the compound $K_4\ Mo(CN)_8, 2H_2O$ in which the molybdenum atom is tetravalent obeys Bose's rule as well, being diamagnetic, as the effective atomic-number of the central molybdenum atom in this case is equal to $(42-4+16)=54$, the atomic number of xenon.

It is therefore of considerable interest to examine magneto-chemically other complex molybdenum compounds with a central molybdenum atom of a different valency. Complex co-ordination compounds of pentavalent molybdenum are known but as it is not easy to obtain them in a magnetically pure form, the study of these compounds was postponed till recently when through the courtesy of Dr. William Wardlaw of Birmingham, I was in possession of a number of these compounds of a degree of purity required for magnetic measurements.

The molecular formulae of these compounds and the results of their susceptibility measurements are given in the following table.

TABLE I.

Compound.	χ_m. 10^6 at 29°	η_{Weiss}.	η_{Bohr} (nearest).
1. $(C_5H_5N)_2$ $MoOCl_5$. Dipyridinium molybdenyl pentachloride.	2·435	8·093	1
2. $(C_5H_5N)MoOBr_4$. Pyridinium molybdenyl tetrabromide.	2·157	8·128	1
3. $(C_5H_5N)_2MoOBr_5$. Dipyridinium molybdenyl pentabromide.	1·550	7·898	1
4. $(C_9H_7N)_2MoOBr_5$. Diquinolinium molybdenyl pentabromide.	1·140	7·257	1
5. $(C_9H_7N)MoOBr_4$. Quinolinium molybdenyl tetrabromide.	1·182	7·96	1

χ_m = mass susceptibility, η_{Weiss} = magneton number, η_{Bohr} = Bohr magneton number.

The physico-chemical properties of these compounds have been studied by James and Wardlaw (*J. Chem. Soc.*, 1927, **131**, 2145). The compounds are much less stable than the trivalent molybdenum complexes. James and Wardlaw attribute their instability to the smaller effective atomic-number of the central molybdenum atom, the number being equal to 49 in these cases—5 units less than that for xenon. The magnetic susceptibilities however at first sight appear to be anomalous being much less than even that for trivalent molybdenum complexes.

There are two ways by which this anomaly can be explained.

In the first place if we assume these pentavalent molybdenum complexes as "perfect" co-ordination complexes, we can attribute to them the following electronic constitution.

TABLE II.

Effective atom No.	Substance.	Number of electrons in different levels.						
		K to M	N_{11} to N_{22}	N_{233}	N_{33}	O_{11}	O_{21}	O_{22}
42	Mo atom	28	8	4		2		
49	Mo Complex	,,	,,	1	6			6
47	Mo Covalent simple	,,	,,	1	6	2		2

The six electrons of N_{33} being coupled with the six of O_2 form the co-ordination bonds. The one lone electron in N_{32} therefore is alone responsible for the paramagnetic susceptibility of the complex, as all the other levels are fully possessed.

Secondly one may view that these complexes are of an imperfect type resembling the double salts ; so that they may be regarded as double compounds of RCl and $MoOCl_3$ held by weak electrostatic attraction. The compound $MoOCl_3$ may reasonably be assumed to possess a co-valent structure whose electronic constitution may be represented as shown in the above table, where N_{32} group remains incomplete having only one electron as before. The two structures thus resemble each other closely so far as the filling up of different levels are concerned. The magnetic susceptibility of $MoCl_5$, of which $MoCl_3$ is a derivative and which evidently possesses a co-valent structure, is approximately equal to one Bohr-magneton (Bose and Mukherjee—private communication). This seems to lend a strong support to this latter view. Which of the two views is more likely to represent the true constitution is difficult to decide at present without a röntgenographic study of the crystals which would throw light on the actual distribution of atoms and groups in the molecule.

My best thanks are due to Dr. William Wardlaw of the University of Birmingham for his kindly supplying me with the samples of the compounds and to Mr. Ramani Mohan Mukherjee of Prof. D. M. Bose's laboratory for measuring the magnetic susceptibilities of the same.

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Reactions at the Surface of Hot Metallic Filaments. Part IV. The Reaction $CO_2+H_2 \rightarrow H_2O+CO$, on Tungsten and Thoriated Tungsten.

By B. S. Srikantan.

In the preceding parts (*J. Indian Chem. Soc.*, 1929, **6**, 931), it has been shown that the interaction of carbon dioxide and hydrogen is to a large extent dependent on the nature of the surface catalysing it. Surfaces which presented a fused or sintered appearance were feebly active compared with fresh surfaces. All these lend support to Taylor's view of active centres (*Proc. Roy. Soc.*, 1925, **108 A**, 105), being mainly responsible for catalysis. In continuation this reaction has been studied on the surfaces of tungsten and thoriated tungsten. The interaction of carbon dioxide and hydrogen on tungsten has been studied by Prichard and Hinshelwood (*J. Chem. Soc.*, 1925, **127**, 1546). But the results described here are more elaborate and contain additional information on the nature of the reaction at the surface of tungsten.

The experimental arrangement was exactly the same as that in the previous parts. The catalyst was a tungsten filament taken from an Osram lamp (106 volts, 60 watts). It was about 60 cm. long and 0·001 cm. in diameter. The optical pyrometer was used to determine the temperatures. A few gas analyses have been performed to show that the reaction is only $H_2+CO_2 \rightarrow CO+H_2O$ and that there is no complication. In the first few experiments it was seen that the resistance of the wire slowly changed such that its temperature changed from 948° to 965° without any adjustment. In the course of these experiments it was also noticed that light blue streaks of tungsten in regular lines corresponding to the shadow of the filament were deposited on the cool sides of the reaction vessel. This is perhaps due to the volatilisation of tungsten as carbonyl which decomposes, depositing tungsten when it comes in contact with the cool sides of the reaction vessel. After this, the deposit did not grow denser and the resistance of the wire was remarkably steady and the results were reproducible. Table I describes the results at 965°.

TABLE I.

P_{CO_2} = 100·8 mm. P_{H_2} = 103·5 mm. Temperature = 965°.

Time (sec.).	Total press (mm.).	Unimolecular constant.
0	204·3	—
300	190·5	0·000476
600	179·0	0·000467
900	169·0	0·000462
1200	160·2	0·000462
1500	152·5	0·000462
1800	146·0	0·000460
2100	104·4	0 000460
	Mean	0·004600

To make sure that no other reaction is proceeding except $H_2+CO_2 \longrightarrow H_2O+CO$, a sample of gas from the last experiment, when the reaction had gone to about 70%, was taken and analysed. Table II shows that no other reaction except the one mentioned is taking place.

TABLE II.

Percentage composition ...	CO_2	CO	H_2	CH_4
By analysis ...	21·09	55·33	23·00	Nil.
By calculation ...	20·99	55·96	23·05	—

Influence of Temperature.—The following table gives the velocity constants at different temperatures with 100 mm. of each of the reacting gases.

TABLE III.

Temperature ...	1060°	1080°	1100°	1280°
Unimol. constant ...	0·00218	0·00280	0·00310	0·00520

Table IV gives the heats of activation and the temperature coefficients calculated from the above tables.

TABLE IV.

Temperature range ...	965°—1080	1060°—1100°	1100°—1280°
Temp. coeff. for 10° ...	1·18	1·09	1·03
Heat of activation (in cal.) ...	54,000	20,000	9,700

The temperature coefficient and the heat of activation fall off with rise of temperature. Similar observations have been recorded in the previous parts (*loc. cit.*). Taylor and Wesely (*J. Phys. Chem.*, 1927, **31**, 216) obtained similar results on the reaction between hydrogen sulphide and sulphur dioxide at glass surfaces. This interesting point will be explained at the end of the paper.

Influence of Pressure of Hydrogen on the Reaction.—Experiments were conducted with 100 mm. of carbon dioxide and varying amounts of hydrogen at a temperature of 1060°. In Table III are given the data for the reaction with equal quantities of the gases. The following tables give the other values. The rate of reaction rapidly increases with the pressure of hydrogen (Fig. 1). In the following tables, the velocity constants have been calculated with reference to carbon dioxide.

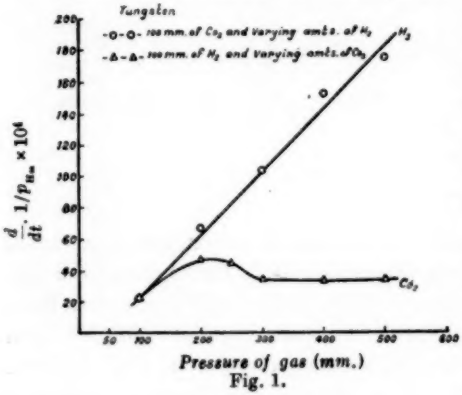

Fig. 1.

TABLE V.

Temperature = 1060°.

P_{CO_2} = 100·5 mm. P_{H_2} = 222·2 mm. $CO_2 : H_2 = 1 : 2$.

Time (sec.)	...	0	30	60	90	120	150	180
Total press. (mm.)	...	323·3	305·8	291·3	278·3	268·0	259·5	252·0
Press. of CO_2 (mm.)	...	100·5	83·0	68·5	55·5	45·2	36·7	29·3
Unimol. constant	...		0·0064	0·0064	0·0066	0·0066	0·0067	0·0067

Mean 0·0066

TABLE VI.

Temperature = 1060°.

P_{CO_2} = 104·5 mm. P_{H_2} = 315·8 mm. $CO_2 : H_2 = 1:3$.

Time (sec.).	Total press. (mm.).	Press. of CO_2 (mm.).	Unimol. const.
0	420·3	104·5	
* —	411·1	95·3	
30	385·9	70·1	0·0102
60	367·5	51·7	0·0102
90	352·4	36·6	0·0106
120	340·6	24·8	0·0113
150	332·1	16·3	0·0116
300	317·0	1·2	
480	309·3		
780	303·0		
1080	298·5		
2880	280·8		

If the reaction is simply a reduction of carbon dioxide to carbon monoxide as represented by $CO_2 + H_2 \longrightarrow H_2O + CO$, it is to be expected that the reaction would stop at about 300 sec., (*cf.* Table VI) when all the carbon dioxide has been used up. But it is seen that the pressure in the system decreases slowly even after 300 sec. in the above experiment. It is possible that another reaction is taking place between carbon monoxide and hydrogen towards the end of the reaction between carbon dioxide and hydrogen. Perhaps this is responsible for the slight rise in the velocity constants towards the end. An analysis of the gas at the end showed the presence of carbon monoxide and hydrogen but not of carbon dioxide. There was the test for the presence of methane of about 2 to 3 per cent. Since the experimental error in the analysis might also be about 2 per cent. it was not taken as conclusive evidence for the presence of methane.

A reaction was carried out with equal quantities of the reacting gases at 1060°, to completion and 100 mm. of hydrogen was put into the system, so that only equal quantities of carbon monoxide and hydrogen remained. No reaction was found to take place. Results similar to those described in Table VI were obtained with 1:4 and 1:5 of carbon dioxide and hydrogen. In both the cases the reaction was allowed to proceed for a long time after the usual limit and the gases analysed. Tests for methane to about 6 to 8 per cent. were obtained. Several analyses were made to detect the

* Time was not noted in the preliminary adjustment of temperature.

presence of methane. The quantities obtained varied with experiments, usually between 5 to 8 per cent. The maximum amount of methane obtained was 8·5 per cent. The production of methane seems to be peculiar and has an important bearing on the mechanism of the reaction. This point will be fully dealt with later. Tables VII and VIII refer to these experiments.

TABLE VII.

Temperature = 1060°.

P_{CO_2} = 103·8 mm. P_{H_2} = 411·3 mm. $CO_2 : H_2 = 1 : 4$.

Time (sec.)	...	0	15	30	46	63	78
Total press. (mm.)	...	515·1	494·0	477·0	462·7	450·6	441·1
Press. of CO_2 (mm.)	...	103·8	82·7	65·7	51·4	39·3	29·8
Unimol. constant			0·0151	0·0152	0·0153	0·0154	0·0160
						Mean	0·0154

The rest of the data is not given here, for those in Tables VI and VII are sufficient to illustrate the above point.

TABLE VIII.

Temperature = 1060°.

P_{CO_2} = 101·0 mm. P_{H_2} = 505·8 mm. $CO_2 : H_2 = 1 : 5$

Time (sec.).	Total press. (mm.).	Pressure of CO_2 (mm.).	Unimol. const.
0	606·8	101·0	
15	583·8	78·0	0·0172
45	554·0	48·2	0·0164
60	541·2	35·4	0·0178
75	531·8	26·0	0·0180
105	519·6	13·8	0·0189
135	512·0	6·2	
255	503·8		
555	495·5		
855	480·4		
3255	453·9		
6255	429·0		

A complete analysis of the gas in the reaction vessel from the previous experiment (Table VIII) is given here.

	C_2H_4 etc.	CO_2	CO	H_2	CH_4	Total
Percentage composition ...			24·9	66·5	8·5	99·9

Influence of Pressure of Carbon dioxide on the Reaction rate.— Experiments were performed with 100 mm. of hydrogen and varying amounts of carbon dioxide at 1060°. In Table III are given the velocity constants with 1 : 1 of hydrogen and carbon dioxide. The following tables give the other values. The reaction at first rises with increase of carbon dioxide till 200 mm. and then falls down to a steady low value. In the following tables the velocity constants are calculated with reference to hydrogen.

TABLE IX.

Temperature = 1060°.

P_{CO_2} = 211·4 mm. P_{H_2} = 105·5 mm. $CO_2 : H_2 = 2 : 1$

Time (sec.).	Total press. (mm.).	Pressure of H_2 (mm.).	Unimolecular constant.
0	316·9	105·5	
* 15	296·4	85·0	
60	280·1	69·0	0·00469
90	271·0	59·8	0·00469
120	263·5	52·8	0·00460
150	256·4	45·2	0·00467
			Mean 0·00466

TABLE X.

Temperature = 1060°.

P_{CO_2} = 258·1 mm. P_{H_2} = 101·2 mm. $CO_2 : H_2 = 2·5 : 1$.

Time (sec.) ...	0	† 60	90	120	150	180	210
Total press. (mm.) ...	359·3	343·9	333·0	324·8	315·8	308·1	302·5
Press. of hydrogen (mm.)	101·2	85·8	74·9	66·7	57·7	50·0	44·4
Unimol. constant ...			0·0045	0·0042	0·0042	0·0045	0·0046
						Mean	0·0044

* Temperature was on the high side to start with and hence it is left out of consideration.

† Temperature on the high side to start with.

TABLE XI.

Temperature = 1060°.

P_{CO_2} = 303·3 mm. P_{H_2} = 100·7 mm. $CO_2 : H_2 = 3 : 1$.

Time (sec.)	...	0	60	120	180	240
Total press. (mm.)	...	404·0	385·5	370·8	358·9	349·8
Pressure of hydrogen	...	100·7	82·2	67·5	55·6	46·5
Unimolecular constant	...		0·00338	0·00334	0·00330	0·00330
					Mean	0·00333

Experiments with carbon dioxide together with four and five times the amount of hydrogen gave the same velocity constants as with 300 mm. of carbon dioxide. The average velocity constant was 0·00333.

The results from the above tables are represented in Fig. 1.

The reaction velocity increases linearly with the pressure of hydrogen. But with carbon dioxide the reaction velocity at first increases slightly, then comes down and remains constant with further increase of carbon dioxide. There is a maximum at about 200 mm. Thus it is evident that the adsorption of hydrogen increases with pressure. But in the case of carbon dioxide the active surface is saturated even below 200 mm. A further increase of CO_2 results in a slight displacement of hydrogen from the surface. But Prichard and Hinshelwood (*loc. cit.*) observed slightly different effects. It was noted by them, however, that saturation for CO_2 was reached at lower pressures than with hydrogen and at higher pressures a slight displacement of hyrogen by carbon dioxide was noted.

It appears therefore that both the reactants are adsorbed on the surface independently of each other. This view is confirmed by the following considerations.

The Active Surface covered with Hydrogen.—The following table has been constructed from the data described above.

TABLE XII.

P_{CO_2} = 100 mm. Temperature = 1060°.

Pressure of hydrogen (mm.)	...	102	223	316	411	506
Percentage of CO_2 converted into CO in 100 sec.	...	25	48	67	83	85

Let θ_{H_2} be the fraction of the active surface covered with hydrogen. Then the adsorption equilibrium is expressed by a simple formula, the percentage conversion of carbon dioxide into carbon monoxide in 100 seconds is taken as proportional to the reaction rate.

$k_1 (1-\theta) [H_2] = k_2\theta$, where $[H_2]$ = the pressure of hydrogen; k_1 and k_2 are constants.

$$\therefore \theta = \frac{[H_2]}{k_2/k_1 + [H_2]} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Let x be the limiting rate at saturation hydrogen pressure.

Then the part of the active surface covered at any pressure is also the ratio of the reaction rate at that pressure to the limiting rate. Thus

$\theta = [H_2]/x$,

if $[H_2] = 102$, $\theta = 25/x$.

if $[H_2] = 223$, $\theta = 48/x$.

Substituting for θ in (1) and solving

$x = 214$; $k_2/k_1 = 771$.

Then

$$\theta_{H_2} = \frac{[H_2]}{771 + [H_2]} \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

The following table gives the fraction of the active surface covered with hydrogen at various pressures. $\theta_{cal.}$ is the value calculated from the equation (2) and $\theta_{obs.}$ is calculated on the assumption that the ratio of the reaction rate at any pressure to that at limiting rate gives the active surface covered at that pressure. They both agree well.

TABLE XIII.

Pressure of hydrogen (mm.)	...	102	223	316	411	506
$\theta_{cal.}$	...	0·12	0·23	0·31	0·36	0·41
$\theta_{obs.}$	...	0·12	0·22	0·29	0·35	0·40

The Active Surface covered with Carbon Dioxide.—The surface is saturated with carbon dioxide even below 200 mm. The following table shows that the limiting rate at saturation pressure is 29 mm. The fraction of the active surface covered with carbon dioxide is given by the expression.—

$$\theta_{CO_2} = \frac{[CO_2]}{16 + [CO_2]}$$

TABLE XIV.

$P_{H_2} = 100$ mm. Temperature = 1060°.

Press. of CO_2 (mm.)	...	103	212	258	303	408	534
Percentage of CO formed in 100 secs.	...	25	48	30	29	29	29
θ cal.	...	0·86	0·93	0·94	0·95	0·96	0·97
θ obs.	...	0·86	1·7	1·0	1·0	1·0	1·0

The Kinetics of the Reaction.—If the gases are adsorbed on the active centres of the surface, independent of each other, it is evident that the reaction rate at any pressure of the gases ought to be a function of the surface covered by hydrogen and also carbon dioxide.

Reaction rate $= k.\ \theta_{H_2} \theta_{CO_2}$,

where k is a constant, θ_{H_2}, θ_{CO_2}, active surfaces covered by H_2 and CO_2 respectively.

Taking the reaction rate as measured by the amount of carbon monoxide formed in 100 secs., the constancy of k can be tested by substituting the data in the above relation. For θ_{H_2} and θ_{CO_2} the observed values from the above table have been used.

TABLE XV.

P_{CO_2} = 100 mm. *Temperature* 1060°. P_{H_2} = 100 mm.

P_{H_2} (mm.).	k	P_{CO_2} (mm.).	k
102	240	103	240
223	240	212	240
316	250	258	250
411	280	303	240
506	250	408	240
		534	240

The idea of independent adsorption of CO_2 and H_2 on the active centres is supported. The reaction seems to proceed through the adsorption of both the gases side by side on the active centres.

The Surface of the Wire.—The fresh wire had a metallic lusture while the wire after use had a dull appearance. Microscopic examination of the surface (Fig. 2) shows that this surface which was smooth has become uneven and pitted after the reaction. This is mostly due perhaps to the volatilisation of tungsten as carbonyl. The shadows on the cool sides of the vessel point to this conclusion. Further the adsorption of the reacting gases on the surface might be of a chemical nature such that the disengagement of the reaction products might involve breaking up of the surface complex and consequent alteration in the nature of the surface.

FIG. 2.

The Mechanism of the Reaction.—In a system containing a number of gases like CO, CO_2 and H_2, it might be expected that the reaction would be very complicated giving various reactions as:—

$$CO_2 + H_2 \rightarrow H_2O + CO,$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O,$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O,$$
$$2CO + 2H_2 \rightarrow CH_4 + CO_2.$$

It is rather surprising that the reaction studied is not so complex but proceeds as $CO_2 + H_2 \rightarrow H_2O + CO$.

Armstrong and Hilditch (*Proc. Roy. Soc.*, 1923, **103A**. 25) state that the reduction of carbon dioxide by hydrogen at the surface of nickel goes directly to methane and gives no carbon monoxide: so that partial reduction is not taking place. " This is at variance with some observations made in the laboratories of the Munitions department in England, during the War, where methane prepared from CO_2 and H_2 contained small percentages of CO" (Rideal and Taylor, "Catalysis in theory and practice," 1926, p. 106, 252).

The results described in the previous tables where the ratio of $H_2 : CO_2$ is more than 2:1, throw some light on the mechanism of the reduction of CO_2 by H_2. There is a slow reaction taking place almost at the end of the usual reaction. Gas analysis showed a small percentage of methane. Several careful analyses were performed. The maximum amount of methane obtained was 8·5 per cent. It is possible to explain the formation of small amounts of methane thus:—

$$CO_2 + H_2 \rightarrow CO + H_2 \quad \ldots \quad \ldots \quad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \ldots \quad \ldots \quad (2)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \ldots \quad \ldots \quad (3)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \ldots \quad \ldots \quad (4)$$

On adding (2) and (3) it comes to the same as (1). It is just possible that as soon as some methane is formed in the presence of carbon dioxide the methane will all be oxidised according to (3). Hence ordinarily no test for methane is got and the sum total of the reactions is as (1). But with excess of hydrogen in the reaction mixture (*cf.* Tables VI to VIII) towards the end when all the carbon dioxide is used up, there is a tendency for methane to accumulate in the system, and hence a slow fall in the pressure is noted. The gas analysis shows the presence of methane: probably a slow reaction represented by (4) is taking place between carbon monoxide and hydrogen. Such a reaction is also possible even in the beginning as soon as some carbon monoxide is formed but then the methane will again be oxidised in the presence of CO_2 (3).

It appeared therefore that the first stage in the reduction of CO_2 is CH_4. The usual reaction is the sum of a series of fast reactions taking place simultaneously.

The possibility of two or more concurrent reactions proceeding at the same time is supported by the experiments on the temperature coefficient of this reaction on this and other wires (*cf.* previous parts). The temperature coefficient and the energy of activation fall off with rise of temperature (*cf.* also Taylor and Wesely, *loc. cit.*). This variation does not arise from the change in the uniformity of the wire and temperature, since these readings have been taken only after the wire was known to be steady and the experiments have been duplicated working at higher and lower temperatures alternately.

In the event of two reactions proceeding at the same time, if the logarithms of the reaction velocity be plotted against the reciprocal of the absolute temperature, one ought not to get a straight line, which would be the case if Arrhenius' equation held good (C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems", 1926, p. 446). Graphs plotted for log K and $1/T$ show that straight lines are not obtained. Fig. 3 gives the graph for tungsten wire. This supports the idea that the reaction studied is made up of more than a single one and whose temperature coefficients are not the same.

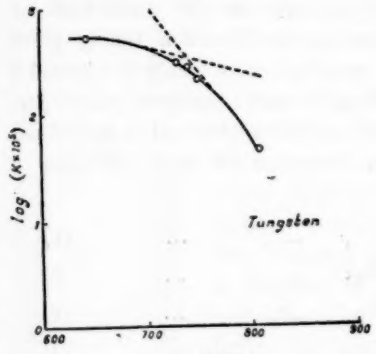

Fig. 3.

Thoriated Tungsten.

A few experiments were next conducted with thoriated tungsten wire as the catalyst, with 100 mm. of each of the gases.

The activity of the wire slowly decreased with use till it came to a low value, where it was steady afterwards. On raising the temperature of the reactions, the wire was again unsteady but gave reproducible results after some use at that temperature. But again working at the lower temperature it did not give the same values as before. The wire was found to have been deactivated to a considerable extent. The wire was heated in vacuum and this again reduced its activity to a considerable extent. But at any temperature it came to a steady

value only after some use: working alternately at high and low temperatures again changed the activity.

At 925° the reaction velocity fell gradually from 0·000507 to 0·000300 where it was steady. At 1025° it fell from 0·000653 to 0·000344 ; but working again at 925° the velocity was only 0·000152. Heating the wire in vacuum and working again at 1025° gave values of 0·00180 only.

The surface of the wire before and after the reaction is similar to that of tungsten.

Summary and Conclusions.

1. The interaction between carbon dioxide and hydrogen has been studied at the surface of tungsten. The wire is steady in activity after some use.

2. The temperature coefficient of the reaction and the engery of activation fall down with rise of temperature.

3. The reaction velocity increases with the pressure of hydrogen.

4. The fraction of the active surface covered with hydrogen at various pressures has been calculated.

5. The surface becomes saturated with carbon dioxide even below 200 mm. pressure and the reaction velocity does not change with further increase of carbon dioxide except for a very slight extent at 200 mm, which is perhaps due to the slight displacement of hydrogen.

6. The reaction proceeds through the adsorption of both the gases on the surface without prejudice to each other.

7. The reaction between carbon dioxide and hydrogen appears to take place through a series of rapid reactions, involving the production of methane and its consequent oxidation to carbonmonoxide by carbon dioxide.

8. The surface of the wire is changed to a decided extent after the reaction.

9. The reaction has also been studied at the surface of thoriated tungsten. The wire was not found to be steady in activity.

In conclusion I wish to express my sincere thanks to Professor H. E. Watson for his kind interest and helpful criticism.

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Preliminary Chemical Examination of *Aegle Marmelos* or the Indian Bel.

By Brij Behari Lal Dikshit and Sikhibhushan Dutt.

Aegle marmelos or the Indian Bel (N. O. *Rutaceae*) is a large deciduous tree which grows throughtout tropical India, mainly in the cultivated state. Its branches are armed with sharp straight spines, 1-2 inches in length. The bark which is nearly half an inch thick has got a soft outer substance broken up into irregular flakes. The wood is yellowish-white in colour, hard and with a strongly aromatic smell when freshly cut. The leaves are alternate and trifoliate and bright green in colour. The flowers are greenish-white, about one inch in diameter and posessing a fine sweet smell. The fruit is 4-6 inches in diameter with a smooth yellowish-grey outer rind which is hard and brittle. The inside of the ripe fruit is filled with a bright yellow, soft pulpy substance having an intense aromatic odour. The seeds which are about ¼-inch long, closely resemble those of the orange and are embedded in the inner core of the pulp inside an outer layer of transparent and exceedingly sticky gum. The taste of the fruit is sweet with a slightly astringent tinge. The gum and the seeds are bitter.

The importance of the Bel tree from the medicinal point of view is very great indeed. Practically every part of it has been used in Indian medicines from time immemorial. There are innumerable references to it in the *Nighanthas* and in the works of Charaka, Sushruta, Mohammed Hossain and more recently of Dymock, Hooker, Kirtikar, Fitzpatric, Lanchester and others. The leaves are made into poultice and used in the treatment of opthalmia and ulcers, and the fresh diluted juice is recommended for catarrh and feverishness. The fresh juice of the leaves is also used along with a few other ingredients in anasarca, costiveness, jaundice, catarrh, fever, delirium and a number of other ailments. A decoction of the roots and bark is sometimes used in the cure of intermittent fever, hypochondriasis, melancholia, palpitation, diarrhoea, gastric irritability and infantile liver. But the greatest medicinal value is ascribed to the fruit, both in ripe and unripe conditions. The

unripe fruit is cut up and sun dried and in this form it is sold in the bazaars. It is regarded as astringent, disgestive, stomachic and specially efficacious in chronic diarrhoea and dysentery, often proving effectual after all other medicines have failed. The ripe fruit is sweet, aromatic, astringent, mild laxative and a good cure for dyspepsia and flatulence.

In view of the facts mentioned above, Bel stands as one of the most important medicinal plants of India, and consequently a systematic analysis was undertaken with a view to study the various chemical ingredients in the different parts of the plants and also as far as possible, to elucidate their chemical constitution. So far as the present authors have been able to ascertain, there has been no work done in this connection up to this time.

Experimental.

The Roots.

The roots are very stiff with a thick bark having a yellowish-white colour and a sharp bitter taste. The woody portion is light yellow when fresh, the colour soon getting bleached by exposure to light and air. The roots were cut up into small bits, dried in the air and extracted with various solvents, in 50-gram lots, in a Soxhlet apparatus. The solvent was subsequently evaporated.

Alcoholic Extract.—It is a dark brown viscous liquid (5·6 %) with a bitter taste, disagreeable smell and greasy feel, and insoluble in water or cold dilute alkalis. On boiling with dilute caustic alkalis it dissolves to a brownish-yellow solution, from which acids precipitate a pasty gelatinous mass with properties practically identical with the original substance. Fehling's solution is slowly reduced on boiling, and an alcoholic solution of the substance yields a transient blue colour with ferric chloride. Concentrated sulphuric acid dissolves it with a blood red colour. The substance appears to contain a glucoside, but none could be isolated.

Chloroform Extract.—A dark brown viscous oil (6·4%) with properties similar to the above.

Petroleum Ether Extract.—It is a clear yellow oil (0·3%) with an extremely bitter taste. It gave no reaction with alkaloid reagents. Fehling's solution was rapidly reduced, but there was no colour with ferric chloride. It is easily soluble in dilute caustic alkalis from which it is precipitated unchanged by acids.

Ether Extract.—6·2 % Similar to the chloroform extract.

Benzene Extract.—6·2%. It is a clear yellow oil with a bitter taste and aromatic smell. Properties are similar to the petroleum ether extract.

Aqueous Extract.—1·7%. It is a viscous brown liquid giving a blue-black colouration with ferric chloride. (Found: Tannin, 0·7 %; reducing sugars, 0·3 %).

Ethyl Acetate Extract.—1·6%. It is a viscous brown oil having properties similar to the alcoholic extract.

Bark.

The bark was stripped from any woody portion that was left, dried, powdered and extracted with various solvents in 50-gram lots. It contains 1·05 % tannin, 1·23 % reducing sugars and 1·66% total sugars estimated as glucose.

Alcoholic Extract.—9·16%. It is a yellowish-green sticky mass smelling strongly of chlorophyll. On treatment with water it is converted into a light green powder by the removal of tannins and sugars. It could not be crystallised. It dissolves in caustic alkalis with an orange-brown colour, from which acids precipitate a yellowish-brown gelatinous mass. Fehling's solution is rapidly reduced and alcholic ferric chloride yields a brownish-red, and alcoholic lead acetate, a dirty green precipitate. It dissolves in concentrated sulphuric acid with a crimson colour. The substance appears to contain a glucoside, but none could be isolated.

Ethyl Acetate Extract.—5·8%. It is a dark green sticky mass which did not yield a solid on treatment with water. Fehling's solution slowly reduced. Alcoholic ferric chloride produces a dark red coloration and alcoholic lead acetate, a dirty green precipitate. Concentrated sulphuric acid produces a reddish-brown colour.

Chloroform Extract.—2·9%. It is a dark green sticky mass with properties similar to the above with the exception of the reaction with strong sulphuric acid in which a violet colour is developed.

Petroleum Ether Extract.—3·6%. It is a light green sticky substance, insoluble in water but soluble in caustic alkalis to a yellow solution from which acids precipitate a milky emulsion. It gave no reaction with Fehling's solution, alcoholic ferric chloride or lead acetate. Concentrated sulphuric acid produces a dark reddish-brown colour.

Ether Extract.—3·8%. It has properties similar to the above.

Benzene Extract.—1·16 %. It has properties similar to the above.

Aqueous Extract.—3·2 %. It is a sticky brown mass consisting mostly of tannins and sugars.

Leaves.

The leaves were dried, powdered and extracted with various solvents. They contain a trace of a volatile oil having the characteristic smell of the leaves and yielding a blue-violet coloration with ferric chloride. They contain 2·1% of tannin, 2·02% of total, and 1·52% of reducing sugars.

Alcoholic Extract.—9·35 %. It is a dark green solid with only a slight sticky consistency and consists mostly of chlorophyll.

Chloroform Extract.—3·72 %. Mostly chlorophyll.

Ethyl Acetate Extract.—5·0 t%. It has properties similar to the alcoholic extract.

Petroleum Ether Extract.—2·1%. It is a pale yellow-green wax, apparently contaminated with chlorophyll. It gave no reaction with Fehlings solution, alcoholic lead acetate or ferric chloride. The substance is insoluble in water or warm dilute caustic alkalis. Concentrated sulphuric acid produces a bright yellow colour. It gives most of the reactions of carotin.

Ether Extract.—6·8 %. It has properties similar to the alcoholic extract.

Benzene Extract.—2·2 %. It is practically identical with the petroleum ether extract.

Aqueous Extract.—8·8%. It is a dark brown syrup which deposits a light brown precipitate on standing. The precipitate consists of calcium and magnesium salts of organic acids and yields on ignition, 13·6% CaO and 18·7% MgO. The mother-liquor contains tannins, sugars, colouring matters together with calcium, magnesium, manganese, iron, aluminium and potassium salts of organic acids. It yields on ignition, 15·25% ash in which the proportion of iron oxide was found to be equal to 6·3%.

Fruit.

The fruit weighs from 250 to 4000 grams. The inside of the unripe fruit consists of a pale yellow pulpy mass, which on breaking up and drying in the air assumes a dark brownish-red colour,

the fully grown but unripe fruit was cut up into small pieces, dried in the sun, powdered and extracted with various solvents.

Alcoholic Extract.—10·8 %. It is a dark red syrup with an intense characteristic smell and a sweetish astringent taste. It is partially soluble in water and completely in dilute caustic alkalis to a yellowish-brown solution. Fehling's solution is slowly reduced and ferric chloride yields a dirty blue coloration. The aqueous solution of the substance decolorises bromine water and aqueous potassium permanganate very readily. It contains 3·7% of reducing and 4·6% of total sugars (on the weight of the dry fruit) estimated as glucose. On ignition it yields 8·6% of ash consisting mostly of calcium, magnesium and iron compounds.

Chloroform Extract.—5·12 %. It is a dark brownish-red syrup with properties similar to the alcoholic extract.

Ethyl Acetate Extract.—5·74 %. This has properties similar to the above.

Ether Extract.—5·9 %. It has properties similar to the above.

Petroleum Ether Extract.—3·82 %. The extract was almost colourless and from this on standing, long colourless needles separated out. These were filtered off and the mother-liquor heated at 100° in a vacuum for about three hours in order to drive off all solvent. The resulting clear brownish-red oil (yield, 3·2%) on examination was found to be of the fixed type (probably derived from the seeds of the (fruit) and gave the following values on analysis:

Specific gravity at 20°	0·930
Saponification value	199·2
Acid value	26·04
Hehner value	94·4
Iodine value	114·5
Acetyl value	nil
ichert value	3·6
Unsaponifiable matter	7·56%

The crystalline substance was recrystallised from dilute alcohol with the addition of animal charcoal in colourless silky needles melting at 103°. It has got interesting physiological and chemical properties which will be the subject of a subsequent communication. The substance has been named "Marmelosin" and is undoubtedly one of the most important active principles of the fruit.

Benzene Extract.—3·1%. It is a brownish-yellow oil from which a trace of marmelosin separates on standing. The oil is identical with that already described.

Aqueous Extract.—4·9%. It is a dark reddish-brown syrup consisting mostly of sugars.

Seeds.

The seeds of the fruit were carefully separated from the pulp by a laborious process and examined. They are exceedingly bitter in taste and contain 11·94% of oil, 17·5% of starch and 12·8% of albuminoids. The oil was extracted from the crushed seeds by petroleum ether and purified by Fuller's earth. When pure it is a light-yellow oil having the following properties.

Moisture	0·8%
Specific gravity at 30°	0·914
Saponification value	195·2
Acid value	1·8
Hehner value	91·3
Iodine value	126·1
Reichert value	2·8
Acetyl value	nil
Unsaponifiable matter	2·7%

The oil burnt with a luminous, slightly sooty, flame and on standing in contact with air, formed an elastic transparent skin on top. Taken internally in doses of 1·5 g. it acts as a very good purgative. The taste of the oil is bitter.

Further work is in progress.

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Studies on some Complex Chromi selenates. Part I.

By Pulin Bihari Sarkar and Sailendra Nath Bhattacharya.

Chromium sulphates, both green and violet, have been exhaustively studied ; complex chromosulphuric acids and their salts have likewise been investigated.

Sulphur and selenium are members of the sixth group of the Periodic Table. They present striking analogy both in the elements themselves and in their salts. Thus the selenates and the sulphates of the alkali metals are perfectly isomorphous. Chromoselenic alums and chromosulphuric alums are also isomorphous. A search for the literature shows that in recent years, like the green and violet chromium sulphates, Meyer (*Z. anorg. Chem.*, 1921, **118**, 1) prepared the corresponding green and violet chromium selenates. The violet salts of chromium are generally the aquo-salts while the green salts are all complex compounds having some negative radicles dissimulated in the complex cation. Beautiful examples of these are to be found in the isomeric hexahydrated chromic chlorides:

$[Cr^{\cdot\cdot\cdot}(H_2O)_6]Cl_3$, violet salt of Recoura;

$[Cr^{\cdot\cdot\cdot}(H_2O)_5\,Cl]Cl_2,H_2O$, green salt of Bjerrum;

$\left[Cr^{\cdot\cdot\cdot}\begin{matrix}(H_2O)_4\\ Cl_2\end{matrix}\right]Cl,\ 2H_2O$, green salt of Recoura.

Green chromium sulphate can combine with one, two or three molecules of sulphuric acid or alkali sulphates to form complex chromosulphuric acids and chromosulphates which have been studied by Recoura (*Compt. rend.*, 1892, **114**, 477).

In the present paper we have studied the formation of chromoselenic acid, chromosulphoselenic acids and their salts. Their composition and chemical properties are exactly similar to those of Recoura's compounds. A study of the dehydration products of pure and mixed chromoselenic alums is in progress. The alums $Cr_2(SeO_4)_3$, $Na_2(SeO_4)_3$, $24H_2O$ and $Cr_2(SO_4)_3$, $(NH_4)_2SeO_4$, $24H_2O$

have been found to lose at 26-27° over sulphuric acid in a desiccator twelve molecules of water of crystallisation. This is in accordance with the behaviour of the other chromosulphuric alums studied by Lowell (*Ann. chim.-phys.*, 1855, *iii*, **44**, 320), Müller-Erzbach (*Z. physikal. Chem.*, 1888, **2**, 113) and Lescœur and Mathurin (*Bull. Soc. chim.*, 1888, **50**, 33).

The alums after dehydration still remain violet. They are soluble in water and in aqueous solution behave as double salts and readily give the tests for the constituent ions. Progressive dehydration at higher temperatures changes the colour to green and although they still remain soluble in water, the reactions of chromium, sulphate or selenate ions are masked in the freshly prepared solution in the cold, as is to be expected. A detailed investigation of this will form the subject of a subsequent communication.

The complex acids and salts already referred to above are all green and hygroscopic crystalline substances, soluble in water, to which they impart the same colour. In the freshly prepared aqueous solution ammonia gives no precipitate of chromium hydroxide, nor does barium chloride precipitate either the selenate or the sulphate ion. But if the cold solution be heated, the respective precipitates may be made to appear, clearly showing that they are all within a complex molecule. The complexes are not, however, very stable, as they break down in solution even at the ordinary room temperature (30°) when kept for about half an hour.

Experimental.

Green chromium selenate has been prepared according to the method of Meyer (*loc. cit.*). It may be mentioned here that Meyer's method for the preparation of violet chromium selenate requires certain modifications as difficulties were experienced in preparing it, no doubt, owing to the rise in temperature.

Preparation of Violet Chromium Selenate.—Five parts of chromium nitrate were dissolved in the least quantity of cold water and then cooled in ice and salt mixture. To it was poured a solution of seven parts of sodium selenate dissolved in the least quantity of water which was also previously cooled in ice and salt. By careful use of a strong freezing mixture, the temperature was kept as low as 0°. Glacial acetic acid was then added drop by drop with frequent stirring during which the temperature was kept below 3°, when crude violet chromium selenate was obtained. It was then dissolved in

the least quantity of cold water and precipitated by 96% alcohol. The process was repeated to get a purer product.

If the temperature be allowed to rise above 10° during the addition of acetic acid or if the acetic acid be added very rapidly, only the green product is obtained.

Preparation of the Chromoselenic Acids and their Salts.—In preparing chromoselenic acid, green chromium selenate and selenic acid were taken in exactly molecular proportions. The chromium selenate was dissolved in the least quantity of water and mixed with the selenic acid and heated on the water-bath to dryness. The residue thus obtained was then dried in an electrically heated air-oven at 120° to constant weight. By employing one, two or three molecular proportions of sulphuric acid or potassium sulphate instead of the selenic acid, in the above process, the corresponding mono-, di-, or tri-sulphoselenic acids or their potassium salts were obtained.

Chromoselenic Acid.—It is a green crystalline substance, soluble in cold water and very hygroscopic. Chromium and selenium cannot be detected in the freshly prepared cold aqueous solution. (Found: Cr, 15·1; Se, 46·2. $HCr(SeO_4)_2$ requires Cr, 15·3; Se, 46·6 per cent.). Its properties clearly indicate that the constitution is $H[Cr(SeO_4)_2]$.

Chromoselenomonosulphuric Acid.—It is a green crystalline powder and very hygroscopic. The chromic, sulphate and the selenate ions are all within a complex ion and therefore a cold freshly prepared solution does not give tests for these ions. (Found: Cr, 16·7; Se, 37·4; SO_4, 15·3. $H_2Cr_2(SeO_4)_3SO_4$ requires Cr, 16·5; Se, 37·4; SO_4, 15·2 per cent.).

The constitution of the compound is

$$H_2\left[\begin{matrix}(Se_4O_4)_3\\ Cr_2(SO_4)\end{matrix}\right].$$

Chromoselenodisulphuric Acid.—It is a green crystalline powder, which rapidly absorbs moisture from the air. Its other properties are also similar to those described above. (Found: Cr, 14·0; Se, 32·5; SO_4, 26·4. $H_4Cr_2(SeO_4)_3(SO_4)_2$ requires Cr, 14·2; Se, 32·5; SO_4, 26·8 per cent.).

The constitution of the compound is

$$H_4\left[\begin{matrix}(SeO_4)_3\\ Cr_2\ (SO_4)_2\end{matrix}\right].$$

Chromoselenotrisulphuric Acid.—It is a green crystalline substance and very hygroscopic. Its other properties are very similar to those described above. (Found: Cr, 13·4; Se, 29·4; SO_4, 35·6. $H_6Cr_2(SeO_4)_3(SO_4)_3$ requires Cr, 13·6; Se, 28·6; SO_4, 35·5 per cent.).

The constitution of the compound is

$$H_6[Cr_2(SeO_4)_3(SO_4)_3].$$

Potassium Chromoselenomonosulphate.—Its properties are very similar to acids but the hygroscopic character is less pronounced. (Found: Cr, 14·9; Se, 33·75; SO_4, 13·4. $K_2Cr_2(SeO_4)_3(SO_4)$ requires Cr, 14·6; Se, 33·52; SO_4, 13·5 per cent.). It is evidently the potassium salt of the acid $H_2\left[Cr_2\begin{matrix}(SeO_4)_3\\(SO_4)\end{matrix}\right]$.

Potassium Chromoselenodisulphate.—It is a green crystalline substance. Its hygroscopic character is less than the corresponding acid. (Found: Cr, 12·0; Se, 26·7; SO_4, 21·8. $K_4Cr_2(SeO_4)_3(SO_4)_2$ requires Cr, 11·8; Se, 26·9; SO_4, 21·7 per cent.).

This compound is the potassium salt of the corresponding acid

$$H_4\left[Cr_2\begin{matrix}(SeO_4)_3\\(SO_4)_2\end{matrix}\right]$$

Potassium Chromoselenotrisulphate.—It is a green crystalline substance and its properties closely resemble those of the corresponding acid. Only its hygroscopic character is less. (Found: Cr, 9·9 : Se, 23·2 ; SO_4, 26·5. $K_6Cr_2(SeO_4)_3(SO_4)_3$ requires Cr, 9·9; Se, 23·4 ; SO_4, 26·3 per cent.).

It is the potassium salt of the acid

$$H_6\left[Cr_2\begin{matrix}(SeO_4)_3\\(SO_4)_3\end{matrix}\right].$$

Incidentally we have prepared a mixed chromosulphoselenic alum which does not seem to have hitherto been described.

Preparation of $Cr_2(SO_4)_3,Na_2(SeO_4),24H_2O$.—Five g. of violet chromium sulphate dissolved in the least quantity of cold water are mixed with 2·4 g. of Na_2SeO_4 likewise dissolved in cold water. The

mixed solution is then allowed to concentrate in vacuum over sulphuric acid. After 24 hours violet octahedral crystals were obtained. They are exactly similar and isomorphous with the other cromoselenic and cromosulphuric alums. Its solution turned green when heated over 60°. (Found: Cr, 10·24; Se, 7·85. $Cr_2(SO_4)_3,Na_2SeO_2,24H_2O$ requires Cr, 10·23, Se, 7·8 per cent.).

Method of Analysis.

Case I. When the compounds contained selenium and no sulphur.—Ammonium hydroxide was added to the aqueous solution and strongly boiled when chromium hydroxide was precepitated which was then filtered, dried and ignited and weighed as Cr_2O_3. The filtrate was then evaporated nearly to dryness with a few c.c. of concentrated hydrochloric acid to reduce the selenates to selenites. Sulphur dioxide was then passed through the solution for some time, when metallic selenium was precipitated which was filtered in a Gooch crucible dried and weighed as such.

Case II. When the compounds contained chromium, selenium and sulphur.—Chromium and selenium were estimated as above. For the estimation of the sulphate radicle a different sample must be taken. The aqueous solution was first boiled with concentrated hydrochloric acid to reduce selenates to selenites, barium chloride solution was then added to precipitate barium sulphate. It was then filtered in a Gooch crucible, washed with alcohol and ether, dried and weighed.

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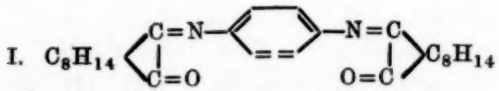
Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. Part IX. (*a*) The Rotatory Dispersion of the Stereoisomeric Oxymethylenecamphors, *p*-Phenylenebisaminomethylenecamphors, and 1 : 4-Naphthylenebisaminomethylenecamphors. (*b*) The Structure of Oxymethylenecamphor and the Kinetics of its Mutarotation.

By Bawa Kartar Singh and Bhutnath Bhaduri.

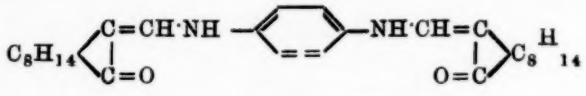
In the present communication we give an account of our experiments on the optical rotatory dispersion of oxymethylenecamphors and their condensation products with aromatic diamines.

Claisen and his co-workers (*Annalen*, 1894, **281**, 331), who discovered *d*-oxymethylenecamphor, also found that this substance undergoes condensation with primary and secondary amines (*loc. cit.*, p. 357). Several of these condensation products were prepared by one of us in 1919 at Lahore, but this work was partly deferred as our studies on the effect of conjugation and position isomerism in the case of derivatives of iminocamphor and bisiminocamphor and their reduction products had not sufficiently advanced. It is now possible to study the effect of conjugation on rotatory power in another way, by comparing the two series of compounds. As in Part VIII, our studies have also been extended to the *l*- and *dl*-isomerides with the object of verifying the assumption of the physical identity of enantiomers.

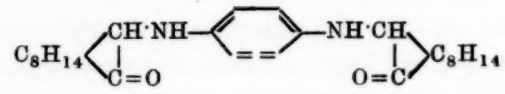
The Effect of Unsaturated Conjugation on Rotatory Power.—On comparing the structural formulae and rotatory power in chloroform of the corresponding derivatives of bisiminocamphor, bisaminomethylenecamphor and bisaminocamphor, striking results emerge:



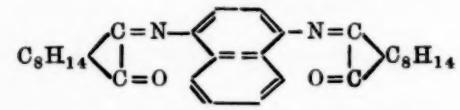
I. $*[M]_D = 6160°$

II. 

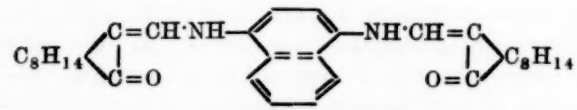
$[M]_D = 2321°$

III. 

* $[M]_D = 469°$

IV. 

* $[M]_D = 8145°$

V. 

$[M]_D = 2746°$

It is thus clear that if the conjugation of the azethenoid groups, involving the carbon atoms of the terpene nucleus and the nitrogen atoms of the side chain is broken (I→III), depression in the rotatory power is phenomenal. The effect is much less marked if the conjugation in the side-chain (*i.e.*, outside the terpene nucleus) is broken (I→II; IV→V).

The Influence of the Chemical Constitution of the Compound and the Nature of Solvent on the Character of Rotatory Dispersion.—The simple dispersion formula of Drude, $[\alpha] = k/(\lambda^2 - \lambda_0^2)$ is valid for a large number of secondary alcohols (Lowry and Dickson, *J. Chem. Soc.*, 1913, **103**, 1067) and for nicotine (Lowry and Singh, *Compt. rend.*, 1925, **181**, 909; Lowry and Lloyd, *J. Chem. Soc.*, 1929, p. 1772) containing only one asymmetric carbon atom. It is also valid up to the extreme limits of our present experimental methods for the methyl*cyclo*hexylideneacetic acid of Pope, Perkin and Wallach (Richards and Lowry, *J. Chem. Soc.*, 1925, **127**, 238)

* These values are taken from Part VIII of this series.

which contains no asymmetric carbon atom. These and other instances show that the simple dispersion formula can be applied to compounds of varied structure. An opportunity is now provided of testing the validity of this simple formula in the case of optically active oxymethylenecamphors and their condensation products with aromatic amino-compounds, in which the elements of simplicity in the molecular structure are absent. These compounds contain two or more asymmetric carbon atoms (*cf.* formulae II and IV) as components of a complex ring system. The striking results of this further test form the subject of the present communication, in which it is shown that in every case the dispersion data can be expressed by a simple equation of the type first put forward by Drude. The remarkable effects which are produced by plotting $1/[\alpha]$ against λ^2 are seen in the very exact straight lines of Figures 1 to 3. A more exact test of the dispersion formula is given by numerical calculation. The tables of rotatory dispersion (VI to XVII) show that the specific rotations, observed and calculated, of oxymethylenecamphor (*d*- and *l*-), *p*-phenylenebisaminomethylenecamphor (*d*- and *l*-), and 1:4-naphthylenebisaminomethylenecamphor (*d*- and *l*-) in different solvents, lie well within the range of possible experimental error. It may be mentioned that oxymethylene-*d*-camphor was first examined in 10 per cent. benzene solution at 20° by Rupe (*Annalen*, 1915, **409**, 327) for 4 wave-lengths from a continuous spectrum (λ=6563, 5898, 5468, and 4861). But he failed to discover any simple linear relation between rotatory power and wave-length. Lowry (*J. Chem. Soc.*, 1919, **115**, 300) first showed that Rupe's results can be expressed as $[\alpha]=\frac{22{\cdot}843}{\lambda^2-0{\cdot}0874}$. This formula agrees with that obtained by us for the equilibrium value after 48 hours (Table VIII), namely, $[\alpha]=\frac{22{\cdot}78}{\lambda^2-0{\cdot}0872}$. The slight differences in the two formulae are due to the different concentrations and temperatures in the two cases. Our observations are made with 12 wave-lengths from a discontinuous spectrum and over a wider range (λ=6708 to 4358) in 4 solvents. We have also extended our observations to the *l*-enantiomer. In alcohol and benzene, the mutarotation of oxymethylenecamphor was slow, and the dispersion formulae of the freshly prepared solution as well as that in which equilibrium had been attained are given (Tables VI, VII, and VIII). In chloroform and pyridine solutions, the mutarotation could not be

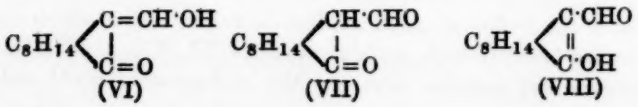
followed owing to its rapidity (Tables IX and X) being almost instantaneous in pyridine, which being basic, acted as a catalyst.

The value of λ_0, the wave-length of the hypothetical absorption band, usually in the ultra-violet region of the spectrum, varies in the initially prepared solution of oxymethylenecamphor and one that has attained equilibrium. In alcohol solution, the value of λ_0 decreases from 2975 to 2788 A.U. on keeping, whereas in benzene solution it increases from 2691 to 2987 A.U. (Tables VI, VII, VIII). This increase and decrease in the wave-length of the ultra-violet absorption band in benzene and alcohol respectively may be correlated with the corresponding increase and decrease in the enol-content of the tautomeric mixture of oxymethylenecamphor in the same two solvents (see Tables IV and V).

p-Phenylenebisaminomethylenecamphor does not show any mutarotation but 1:4-naphthylenebisaminomethylenecamphor shows slight in chloroform but not in other solvents (Tables XI to XVII).

It may be observed that the rational way of determining the effect of constitution on rotatory power in organic compounds is to study the rotatory dispersion and not to be content with making observations for one wave-length only. To take only two instances from the present data: the specific rotatory power of *p*-phenylenebisaminomethylenecamphor in chloroform solution is lower than that for 1:4-naphthylenebisaminomethylenecamphor for Hg_{5461} line but it becomes almost identical for Li_{6708} (Tables XI and XIII). On the other hand, this value is almost identical in pyridine for the two compounds for Hg_{5461} and it is higher for *p*-phenylenebisaminomethylenecamphor for Li_{6104} (Tables XII and XVI). These observations serve to show the inadequacy of deducing the effect of constitution on rotatory power from observations confined to a single wave-length. It is thus clear that only the rotatory dispersion of a compound can give a true picture of the effect of constitution on its rotatory power.

The Structure of Oxymethylenecamphor and the Kinetics of the Chemical Change involved in its Mutarotation.—Claisen (*loc. cit.*) suggested the following structural formulae for oxymethylenecamphor.



(VI) (VII) (VIII)

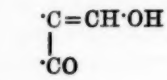
Brühl (*Z. physikal. Chem.*, 1900, **35**, 1), from refractometric determinations, and Federlin (*Annalen*, 1907, **356**, 251), from colorimetric data decided in favour of the structure (VI). Pope and Read (*J. Chem. Soc.*, 1909, **95**, 175) explained the mutarotation of oxymethylenecamphor by assuming that it is a mixture of the two isodynamic forms (VI and VIII). They arrived at this conclusion from the experimental results of Brühl and Federlin. This view of Pope and Read seems to be disproved by the measurements of the percentage of keto- and enol-quantities in oxymethylenecamphor by Meyer's method (*Annalen*, 1911, **380**, 212; *Ber.*, 1911, **44**, 2718; 1912, **45**, 2843). In a freshly prepared benzene solution of oxymethylenecamphor, the percentage of enol at 35° is 32 ; it increases to 81 in five to six hours (Table IV). This shows that there is a considerable amount of the keto-form in a freshly prepared solution. This result is in agreement with the observations of previous workers who found benzene to be an enolising and alcohol to be a ketonising solvent (Wislicenus, *Ber.*, 1899, **32**, 2837; Brühl, *Ber.*, 1899, **32**, 2326 ; Meyer, *loc. cit.*; *Ber.*,1910, **43**, 3044). The value of the velocity constant of mutarotation of oxymethylenecamphor in benzene is nearly identical with that obtained from the progressive determinations of the relative amounts of the enol- and keto-modifications present in the tautomeric mixture by Meyer's method referred to above (Tables I and IV). The close agreement in the value of the velocity constant obtained by these two independent methods conclusively shows that the chemical change involved in the mutarotation of oxymethylenecamphor is of the keto-enol type, and may be represented by the schemes VII⟶VI or VII⟶VIII, or by both these changes taking place simultaneously. It is thus clear that the keto-form (VII) is one of the constituents of the tautomeric mixture. The above-mentioned changes are of the monomolecular type, as has been found by experiment. The prototropic changes involved in the mutarotation process are reversible in character. It may therefore be assumed that in benzene solution of oxymethylenecamphor, equilibrium exists between all the three forms. The temperature-coefficient of the velocity constant of mutarotation of oxymethylenecamphor in benzene ($K_{45°}/K_{35°}$) is approximately 29·3 (Table III), being nearly ten times as large as that for an ordinary chemical reaction. It thus appears that the keto-modification of oxymethylenecamphor is very unstable in benzene solution.

The value of the velocity constant of mutarotation of oxymethylene-*l*-camphor for Hg_{green} and Hg_{yellow} lines is identical (Table II).

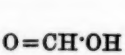
The percentage of enol-modification of oxymethylenecamphor in alcohol at 35° was found to be 95·5 in a freshly prepared solution, which falls to 88 in four hours and then remains constant (Table V). Sen and Mondal (*J. Indian Chem. Soc.*, 1928, **5**, 609) working at lower temperature (27°) found the enol-percentage in a freshly prepared alcoholic solution of oxymethylenecamphor to be over 98 which decreased to 81 on the fourth day. It thus appears that a freshly prepared alcoholic solution of the substance consists of 100 per cent. enol, specially at a lower temperature. The mutarotation of the substance in alcohol may be represented by one of the following schemes:—VI⟶VII; VIII⟶VII; VI⟶VII⟶VIII (or *vice versa*).

It has not been possible to calculate the velocity constant of the mutarotation of oxymethylenecamphor in alcohol owing to the very slight decrease in the angle of rotation in the course of 28 hours (see Table VB).

The substance has a definite melting point and crystalline form. It may therefore be assumed that it is homogeneous in the solid state and may be represented by one of the two enolic constitutions (VI or VIII), and in all probability it is constituted as (VI), on account of its acidic character. This structure of oxymethylenecamphor resembles that of formic acid:*



Oxymethylene compounds.



Formic acid.

Since formic acid is much stronger than any other aliphatic acids it may be concluded that the keto-enol form (VI), would be more acidic than the alternative aldo-enol form, (VIII).

The Physical Identity of Enantiomers.—The fact that the rotatory dispersion of the *d*- and *l*-isomerides can be expressed by the same equation is a strong proof of the identity of enantiomers, so

* For the above-mentioned analogy of formic acid to oxymethylene compounds, we are indebted to Dr. J. C. Bardhan (*private communication*).

far as the magnitude of rotatory power is concerned. The differences in the observed values of rotation for the *d*- and *l*-isomerides are well within experimental error (Tables VI, VII; XI to XVII). The velocity constant of mutarotation of the *d*- and *l*-oxymethylenecamphor in benzene is practically identical (Tables I and II). This shows that the identity of enantiomers with respect to their physical properties (such as rotatory power) extends also to the rate of chemical change involved in the mutarotation of the enantiomers.

The racemic forms of *p*-phenylenebisaminomethylenecamphor and 1 : 4-naphthylenebisaminomethylenecamphor melt at higher temperature than their optically active isomerides. It follows therefore that the racemic forms are true *dl*-compounds, at least in the solid state.

We wish to reserve the further study of the condensation products of oxymethylenecamphors with amines with the object of elucidating (*a*) the effect of unsaturated conjugation and position isomerism on optical rotatory power, (*b*) the character of rotatory dispersion and (*c*) the extent of the physical identity of enantiomers. The results of this work will be given in subsequent communications.

Experimental.

Oxymethylenecamphor (d-, l-, dl-).

The d-*isomer* was prepared by the method of Bishop, Claisen, and Sinclair (*Annalen*, 1894, **281**, 331).

The l-*isomer* was prepared from *l*-camphor in the same way and exhibited properties corresponding with those of its *d*-isomeride. This substance has also been prepared by the same method by Pope and Read (*J. Chem. Soc.*, 1913, **103**, 444), who do not give any analytical data. (Found: C, 73·13; H, 8·99. $C_{11}H_{16}O_2$ requires C, 73·34; H, 8·89 per cent.).

"*Externally compensated oxymethylenecamphor*" was prepared from *dl*-camphor in the same way as its optically active isomerides and has the same crystalline form and similar solubility but melts at 77°-78°. (Found: C, 73·14; H, 8·97. $C_{11}H_{16}O_2$ requires C, 73·34; H, 8·89 per cent.).

Pope and Read (*loc. cit.*) also prepared this substance by mixing equal weights of the two components (*d*- and *l*-) and found its melting point 80°-81°. We have also prepared it in the same way but find its melting point, 78-79°.

The Velocity of Mutarotation of Oxymethylenecamphor (d- *and* l-) *and the Order of the Reaction.*—The velocity constant was determined in benzene at 35° and the reaction was found to be monomolecular; the results obtained are recorded below:

TABLE I.

*Oxymethylene-*d*-camphor.*

Solvent = benzene; temp. = 35°; length of tube = 2 dcm.

The value of K, the velocity constant, is calculated from the monomolecular formula, $K = \frac{2{\cdot}303}{t_y - t_x} \log \frac{[\alpha]_x - [\alpha]_\infty}{[\alpha]_y - [\alpha]_\infty}$, the time being expressed in seconds.

	Concentration: g/100 c.c.	Time (minutes).	$[\alpha]_{Hg}$ (gr.)	$K \times 10^4$.
1st Sample.	1·0008	Initial	Not observed	—
		30	174·9°	—
		63·5	151·4	1·969
		96·5	135·9	1·976
		128	125·9	1·888
		159	119·0	1·938
		∞	103·0	—
2nd Sample		(after 48 hrs.)	Mean	1·944
	0·9975	0	209·0°	—
		31	177·4	1·988
		63·5	154·9	1·919
		99.5	137·3	1·995
		134·5	126·3	1·961
		169·5	120·3	1·945
		218·5	113·8	1·842
		278·5	109·3	1·919
		∞	104·7	—
		(after 48 hrs.)	Mean	1·938

TABLE II.

*Oxymethylene-*l*-camphor.*

Solvent = benzene ; temp. = 35° ; length of tube = 2 dcm.

	Concentration, g./100 c. c.	Time (minutes).	[α].	$K \times 10^4$.
	1·0000	Initial.	Not observed.	—
		25	−183·0°	—
		54	−160·5	1·927
Hg_{green}		84·5	−143·5	1·954
		114·5	−132·0	1·911
		142·5	−124·5	1·849
		172·5	−118·5	1·923
		∞	−104·0	—
		(after 48 hrs.)	Mean	1·913

TABLE II—*Continued.*

	Concentration : g./100 c. c.	Time (minutes).	[α].	$K \times 10^4$.
	1·0000	Initial.	Not observed.	
		25	−157·0°	—
		55·5	−137·0	1·938
		84·5	−123·5	1·945
Hg_{yellow}		115·5	−113·5	1·904
		150	−106·0	1·858
		182	−101·0	1·919
		∞	− 90·0	—
		(after 48 hrs.)		Mean 1·913

Mean value of $K_{35}°$ (from Tables I and II) $= 1·927 \times 10^{-4}$.

The velocity constant for the mutarotation in benzene was determined also at 45°. The velocity of the change was so high that the equilibrium was attained within 15 minutes of the preparation of the solution.

TABLE III.

Oxymethylene-d-camphor.

Solvent = benzene ; temp. = 45° ; length of tube = 2 dcm.

	Concentration : g./100 c. c.	Time (seconds).	[α].	$K \times 10^3$.
1st Sample.	1·0252	0	127·2°	—
		60	116·5	6·265
		110	110·2	6·265
Hg_{green}		200	103·3	5·801
		240	101·4	5·158
		290	99·42	5·504
		∞	93·1	—
2nd Sample.	1·0000	(after 6 hrs.)		Mean ·5798
		0	137·0°	93·1
		45	128·0	5·665
		85	122·0	5·389
		127	117·0	5·297
		177	112·0	5·757
		233	108·0	5·502
		279	105·5	5·597
Hg_{green}		329	103·5	5·367
		395	101·5	5·527
		∞	97·0	—
		(after 6 hrs).		Mean 5·512

Mean value of $K_{45}° = 5·655 \times 10^{-3}$ and $K_{45}°/K_{35}° = 29·3$.

Determination of the Relative Amounts of Enol- and Keto-modifications Present in the Tautomeric Mixture of Oxymethylene-d-camphor in Benzene and Alcohol at 35°.—The experiment was carried out by adding rapidly an alcoholic solution of bromine (the strength

of which was not determined) to the solution of the substance (10 c. c.) cooled to $-7°$, until the colour was no longer discharged. The excess of bromine was removed by the addition of an alcoholic solution of β-naphthol, excess of potassium iodide was then added, and after warming gently at 50-55°, the free iodine was determined by standard thiosulphate solution.

TABLE IV.

Oxymethylene-d-camphor.

Solvent = benzene ; sodium thiosulphate = $1{\cdot}015N/10$.

The value of K is calculated from the monomolecular formula given in Table I and substituting v for a.

	Concentration : g./100 c. c.	Time (minutes).	Thiosulphate.	Enol.	$K \times 10^4$.
1st Sample.	0·9999	0	3·45 c. c.	31·49%	—
		33	5·30	48·42	2·118
		68	6·55	59·82	2·065
		123	7·7	70·34	2·100
		177	8·25	75·37	2·007
		∞	8·85	80·83	—
		(after 6 hrs.)			Mean 2·072
2nd Sample.	0·9975	0	3·55	32·51	—
		36	5·55	50·83	2·168
		96	7·40	67·76	2·230
		156	8·51	74·64	1·185
		∞	8·90	81·51	—
		(after 6 hrs.)			Mean 2·123

Mean value of $K_{35°} = 2{\cdot}10 \times 10^{-4}$.

TABLE V.

Oxymethylene-d-camphor.

Solvent = ethyl alcohol ; sodium thiosulphate = $1{\cdot}015N/10$.

A. Concentration : g./100 c. c.	Time.	Thiosulphate.	Enol.
1·0004	0 min.	10·45 c. c.	95·45%
	88 ,,	9·85	89·97
	180 ,,	9·70	8·61
	255 ,,	9·65	88·14
	24 hrs.	9·65	88·14
	48 ,,	9·65	88·14

TABLE V—*Continued.*

Length of the tube.	Concentration : g./100 c. c.	Time.	$\alpha^{\overline{5461}}$ Hg (gr.)	$[\alpha]^{5461}$ Hg (gr.)
2 dcm.	1·0004	0 mins.	4·71°	235·4°
		41 ,,	4·68	233·9
		124 ,,	4·65	232·4
		221 ,,	4·61	230·0
		28 hrs.	4·54	226·4

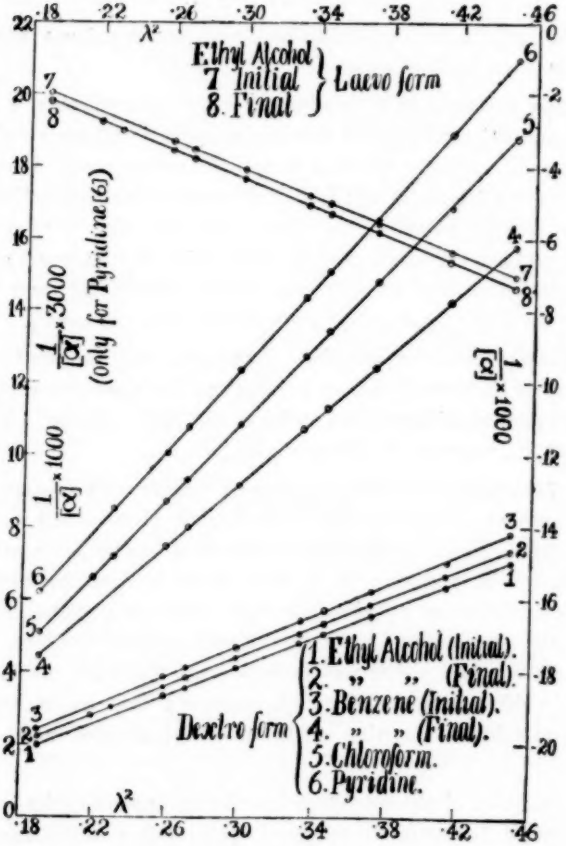


Fig. 1.

Rotatory Dispersion of Oxymethylenecamphor (d *and* l)

p-*Phenylenebisaminomethylene*-d-*camphor* (II).—Oxymethylene-*d*-camphor (0·9 g.) dissolved in alcohol (4—5 c. c.) and *p*-phenylenediamine (0·3 g.) dissolved in 30% acetic acid (4—5 c. c.) were mixed together when a pale yellow precipitate came down immediately. The precipitate was crystallised out of absolute alcohol (after boiling with a little charcoal) as light yellow needles, m. p. 269°-71° (yield, 0·65 g.). It is fairly easily soluble in pyridine ; less so in chloroform ; difficultly soluble in benzene, acetone ; still less soluble in ethyl alcohol and methyl alcohol. (Found: C, 77·77 ; H, 8·34. $C_{28}H_{36}O_2N_2$ requires C, 77·78 ; H, 8·33 per cent.).

The chloroform solution (initially of pale yellow colour) turns to deep scarlet red in 30 minutes.

Rotatory power could be determined in two solvents only, namely, pyridine and chloroform, as it was too insoluble in others to observe the rotation accurately ; rotation in pyridine being greater than that in chloroform (Tables XI and XII). p-*Phenylenebisamimonethylene*-l-*camphor* was prepared in the same way as the corresponding *d*-isomer and has the same melting point, solubility, etc; and also the same rotation within experimental error (Tables XI and XII). (Found: N, 6·65. $C_{28}H_{36}O_2N_2$ requires N, 6·48 per cent.).

p-*Phenylenebisaminomethylene*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 273°-75°. (Found: N, 6·65. $C_{28}H_{36}O_2N_2$ requires N, 6·48 per cent.).

1:4-*Naphthylenebisaminomethylene*-d-*camphor* (V).—Oxymethylene-*d*-camphor (0·9 g.) dissolved in alcohol (4—5 c. c.) and 1:4-naphthylenediamine hydrochloride dissolved in 30% acetic acid (4—5 c. c.) in presence of a little fused sodium acetate, were mixed together when a yellowish-green precipitate came down at once. The precipitate was crystallised out of absolute alcohol (charcoal) as yellowish-green prisms, m.p. 203°-4°. It is easily soluble in chloroform, pyridine and benzene ; less so in acetone ; difficultly soluble (in the cold) in ethyl alcohol and methyl alcohol.

The solution of the substance in ordinary organic media is strongly fluorescent (green in the reflected light ; yellow in the transmitted light), the fluorescence is however not so marked in ethyl alcohol and methyl alcohol. (Found: N, 6·12. $C_{32}H_{38}O_2N_2$ requires N, 5·81 per cent.).

The order of rotatory power in different solvents (Tables XIII to XVII) is as chloroform > acetone, ethyl alcohol > pyridine > benzene.

Rotation in methyl alcohol could not be determined as the substance was very difficultly soluble in the solvent at 35°.

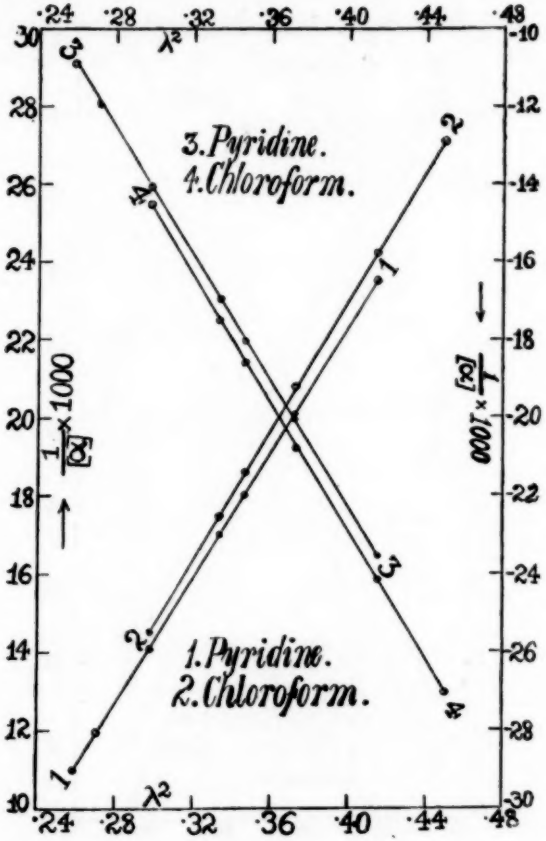


Fig 2,

Rotatory dispersion of p-*phenylenebisaminomethylene*-d-*camphor*.

d, 1, 2.
l, 3, 4.

1 : 4- *Naphthylenebisaminomethylene*-l-*camphor* was prepared in the same way as the corresponding *d*-compound and has the same m.p., crystalline form and solubility. (Found: N, 6·05. $C_{32}H_{38}O_2N_2$

requires N, 5·81 per cent.). The rotatory power is identical with that of the *d*-isomeride within experimental error (Tables XIII to XVII).

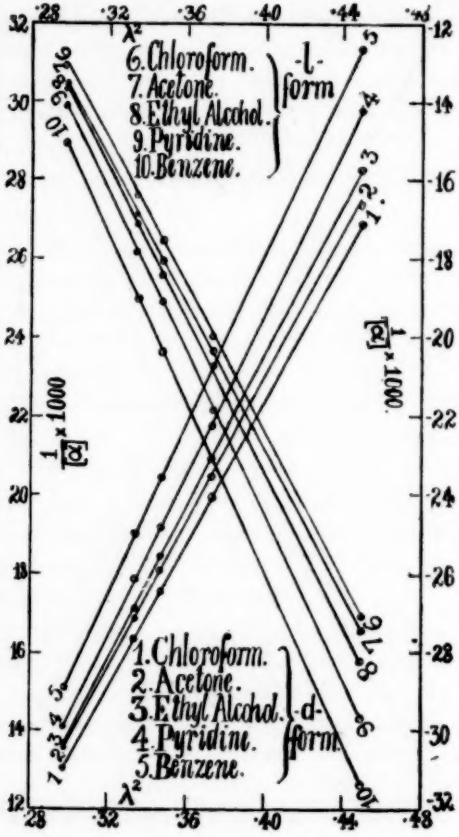


FIG. 3.

Rotatory Dispersion of 1 :4-*Naphthylenebisaminomethylenecamphor* (d- *and* l-).

1:4-*Naphthylenebisaminomethylene*-dl-*camphor* was prepared in the same way as its optically active isomers and has the same crystalline form and similar solubility but melts at 220°-222°. (Found: N, 6·07. $C_{32}H_{38}N_2O_2$ requires N, 5·81 per cent.).

The rotatory power determinations were made in a 2 dcm. jacketed tube at 35°. The value of λ_0, calculated from the dispersion formula, is given in the tables, and is expressed as μ, or 10^{-4} cm.

TABLE VI.

Oxymethylenecamphor.

Solvent = ethyl alcohol (*initially*).

$$[\alpha] = \pm \frac{51{\cdot}18}{\lambda^2 - 0{\cdot}0885}; \quad \lambda_0 = 0{\cdot}2975.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line (λ in A.U.).	[α]calc. =C.	[α]obs. =O′.	O′−C.	Concn. g./100 c.c.
0·4980	−1·0°	+504·0°	Hg_{4358}	±505·0°	−505·3°	+0·3°	0·5008
0·4992	−0·4	300·5	Cd_{5086}	300·9	−301·0	+0·1	0·5000
,,	+0·4	280·4	Ag_{5209}	280·0	−279·0	−1·0	,,
0·4980	−1·0	243·1	Hg_{5461}	244·1	−243·6	−0·5	0·5008
,,	+0·4	208·8	Hg_{5780}	208·4	−207·7	−0·7	,,
0·5000	+0·8	198·5	Na_{5893}	197·7	−198·2	+0·5	0·5020
0·5004	−0·2	179·9	Li_{6104}	180·1	−179·4	−0·7	0·4984
0·4992	+0·2	157·2	Cd_{6438}	157·0	−157·0	±0	0·5000
0·5004	−0·7	140·9	Li_{6708}	141·6	−142·4	+0·8	0·4984

As the substance undergoes mutarotation, a fresh solution was prepared for each wave-length and rotatory power measurements were made within ten minutes of making up the solution.

TABLE VII.

Oxymethylenecamphor.

Solvent = ethyl alcohol (*after* 24 *hours*).

$$[\alpha] = \pm \frac{50{\cdot}67}{\lambda^2 - 0{\cdot}0777}; \quad \lambda_0 = 0{\cdot}2788.$$

Dextro					*Laevo*		
Conc. g./100 c.c	O−C.	[α]obs. =O.	Line (λ in A.U.).	[α] calc. =C.	[α] obs. =O′.	O′−C.	Concn. g./100 c.c.
0·4980	+1·2°	+452·8°	Hg_{4358}	±451·6°	−451·3°	−0·3°	0·4996
0·5004	−1·1	357·8	Cd_{4678}	358·9	358·3	−0·6	,,
,,	−1·1	330·8	Cd_{4800}	331·9	332·3	+0·4	,,
,,	−0·1	279·9	Cd_{5086}	280·0	280·2	+0·2	,,
,,	+1·2	262·9	Ag_{5209}	261·7	262·2	+0·5	,,
0·4980	+0·1	229·9	Hg_{5461}	229·8	229·2	−0·6	,,
0·5004	−1·1	227·9	Ag_{5468}	229·0	−	−	,,
0·4980	+0·6	197·8	Hg_{5780}	197·2	197·2	±0	,,
0·5000	+0·1	188·0	Na_{5893}	187·9	187·2	−0·7	,,
0·5004	+0·1	171·9	Li_{6104}	171·8	172·1	+0·3	,,
,,	−0·6	149·9	Cd_{6438}	150·5	151·1	+0·6	,,
,,	+0·8	136·9	Li_{6708}	136·1	136·1	±0	,,

TABLE VIII.

*Oxymethylene-*d*-camphor in Benzene.*

Initially.

$$[\alpha] = \frac{48{\cdot}39}{\lambda^2 - 0{\cdot}0724}; \quad \lambda_0 = 0{\cdot}2691.$$

After 48 *hours.*

$$[\alpha] = \frac{22{\cdot}78}{\lambda^2 - 0{\cdot}0892}; \quad \lambda_0 = 2987.$$

Conc. g 100 c.c.	O−C.	[α] calc. =C.	[α] obs. =O.	Line.	[α] obs. =O′.	[α] calc. =C′.	O′−C′.	Conc. g/100 c.c.
0·4992	+1·9°	+411·8°	+413·7°	Hg_{4358}	+227·4°	+226·2°	+1·2°	0·4992
0·4996	−0·5	259·7	259·2	Cd_{5086}	134·2	134·4	−0·2	,,
,,	−0·1	243·3	243·2	Ag_{5209}	125·2	125·1	+0·1	,,
0·4992	±0	214·3	214·3	Hg_{5461}	109·1	109·0	+0·1	,,
,,	+0·4	184·9	185·3	Hg_{5780}	93·1	93·0	+0·09	,,
0·5000	±0	176·0	176·0	Na_{5893}	88·1	88·2	−0·14	,,
0·5004	−1·3	161·2	159·9	Li_{6104}	80·1	80·3	−0·24	,,
,,	+0·4	141·5	141·9	Cd_{6438}	70·1	70·0	+0·09	,,
,,	−0·2	128·1	127·9	Li_{6708}	63·1	63·1	−0·02	,,

TABLE IX.

Oxymethylene-d-camphor in Chloroform (after 24 hours).

$$[\alpha] = \frac{18{\cdot}80}{\lambda^2 - 0{\cdot}0947}; \quad \lambda_0 = 0{\cdot}3078.$$

Concentration. g./100 c.c.	Line.	[α] obs. = O.	[α] calc. = C.	O−C.
0·4980	Hg_{4358}	+196·8°	+197·5°	−0·7°
,,	Cd_{4678}	151·6	151·6	±0
,,	Cd_{4800}	139·5	138·6	+0·9
,,	Cd_{5086}	114·5	114·7	−0·2
,,	Ag_{5209}	107·4	106·4	+1·00
,,	Hg_{5461}	92·37	92·34	+0·03
,,	Hg_{5780}	78·30	8·54	−0·24
,,	Na_{5893}	74·29	74·49	−0·20
,,	Li_{6104}	67·26	67·66	−0·40
,,	Cd_{6438}	59·23	8·79	+0·44
,,	Li_{6708}	53·21	52·91	+0·30

The mutarotation in chloroform is too rapid to observe readings accurately in the initial stages; so much so that the initial rotation $[\alpha]_{Hg(gr)} = 172{\cdot}7°$ falls to 108·4° in course of 20 minutes, the equilibrium value 92·37° being attained in next half an hour or so.

TABLE X.

Oxymethylene-d-camphor in Pyridine.

$$[\alpha] = \frac{52{\cdot}85}{\lambda^2 - 0{\cdot}0811}; \quad \lambda_0 = 0{\cdot}2848.$$

Concentration : g./100 c.c.	Line.	[α]obs. = O.	[α]calc. = C.	O−C.
0·5008	Hg_{4358}	+484·2°	+485·2°	−1·0°
,,	Cd_{4800}	353·4	353·9	−0·5
,,	Cd_{5086}	297·5	297·8	−0·3
,,	Ag_{5209}	278·6	277·8	+0·8
,,	Hg_{5461}	242·6	243·4	−0·8
,,	Hg_{5780}	208·6	208·8	−0·2
,,	Na_{5893}	198·7	198·6	+0·1
,,	Li_{6104}	181·7	181·3	+0·4
,,	Cd_{6438}	158·7	158·3	+0·4
,,	Li_{6708}	142·7	143·3	−0·6

Initial and final readings were the same.

TABLE XI.

p-Phenylenebisaminomethylenecamphor in Chloroform.

$$[\alpha] = \pm \frac{11\text{ }\cdot 3}{\lambda^2 - 0\cdot 1254}; \quad \lambda_0 = 0\cdot 3542.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line.	[α]calc. =C.	[α]obs. =O′.	O′−C.	Concn. g./100 c.c.
0·0820	−1·5°	+689·2°	Hg_{5461}	±690·7°	−690·2°	−0·5°	0·0804
,,	+1·4	573·2	Hg_{5780}	571·8	572·2	+0·4	,,
,,	−1·2	536·7	Na_{5893}	537·9	537·5	−0·4	0·0800
0·0800	−1·4	481·3	Li_{6104}	482·7	480·3	−2·4	0·0812
,,	−0·3	412·5	Cd_{6438}	412·8	413·5	+0·7	,,
,,	+1·0	368·7	Li_{6708}	367·7	369·5	+1·8	,,

The solution initially of pale yellow colour changes to scarlet red with time. Readings were taken with fresh solutions almost with every line.

TABLE XII.

p-Phenylenebisaminomethylenecamphor in Pyridine.

$$[\alpha] = \pm \frac{124\cdot 8}{\lambda^2 - 0\cdot 1225}; \quad \lambda_0 = 0\cdot 3500.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line.	[α]calc. =C.	[α]obs. =O′.	O′−C.	Concn. g./100 c.c.
0·0800	−3·1°	+912·5°	Cd_{5086}	±915·6°	−917·5°	+1·9°	0·0812
,,	−0·6	837·5	Ag_{5209}	838·1	837·3	−0·8	,,
,,	+2·6	712·5	Hg_{5461}	709·9	710·9	+1·0	0·0816
,,	−1·8	587·5	Hg_{5780}	589·3	588·3	−1·0	,,
,,	+1·4	556·3	Na_{5893}	554·9	554·2	−0·7	0·0812
,,	+1·4	500·0	Li_{6104}	498·6	498·7	+0·1	,,
,,	−1·8	425·0	Cd_{6438}	426·8	424·8	−2·0	,,

There was no mutarotation or change in colour with lapse of time (compare the same in chloroform).

TABLE XIII.

1:4-*Naphthylenebisaminomethylenecamphor in Chloroform.*

$$[\alpha] = \pm \frac{109{\cdot}0}{\lambda^2 - 0{\cdot}1558}; \quad \lambda_0 = 0{\cdot}3947.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line.	[α]calc. =C.	[α] obs. =O′.	O′−C.	Concn. g./100 c.c.
0·0808	+2·2°	+767·4°	Hg_{5461}	±765·2°	−764·9°	−0·3°	0·0804
,,	+1·5	612·6	Hg_{5780}	611·1	609·4	−1·7	,,
0·0800	−0·3	569·4	Na_{5893}	569·7	569·9	+0·2	0·0816
0·0808	−1·2	501·3	Li_{6104}	502·5	500·0	−2·5	0·0800
,,	+1·0	371·4	Li_{6708}	370·4	368·8	−1·6	,,

The chloroform solution undergoes slight mutarotation, the initial value $[\alpha]_{Hg(5461)} = 767{\cdot}4°$ changing to 730·4° in course of two and a half hours. After 24 hours the colour was too dark to be read.

TABLE XIV.

1:4-*Naphthylenebisaminomethylenecamphor in Acetone.*

$$[\alpha] = \pm \frac{108{\cdot}9}{\lambda^2 - 0{\cdot}1506}; \quad \lambda_0 = 0{\cdot}3881.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line.	[α]calc. =C.	[α] obs. =O′.	O′−C.	Concn. g./100 c.c.
0·0800	−0·4°	+737·5°	Hg_{5461}	±737·9°	−737·5°	−0·4°	0·0800
,,	+0·5	593·8	Hg_{5780}	593·3	593·8	+0·5	,,
0·0804	−0·7	553·5	Na_{5893}	554·2	554·2	±0	0·0812
0·0808	−1·6	488·9	Li_{6104}	490·5	491·5	+1·0	0·0824
,,	+1·7	365·4	Li_{6708}	363·7	364·1	+0·4	,,

There was no mutarotation observed on keeping the solution for 24 hours, though the solution had acquired red colour.

TABLE XV.

1:4-*Naphthylenebisaminomethylenecamphor in Ethyl Alcohol.*

$$[\alpha] = \pm \frac{103{\cdot}5}{\lambda^2 - 0{\cdot}1571} \; ; \; \lambda_0 = 0{\cdot}3964.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line.	[α]calc. =C.	[α]obs. =C′.	O′−C.	Concn. g./100 c.c.
0·0804	+0·3°	+733·8°	Hg_{5461}	±733·5°	−734·4°	+0·9°	0·0800
,,	−0·1	584·5	Hg_{5780}	584·6	584·4	−0·2	,,
0·0800	−0·8	543·8	Na_{5893}	544·6	543·8	−0·8	,,
0·0804	−1·5	478·8	Li_{6104}	480·3	481·6	+1·3	0·0824
,,	+1·1	354·5	Li_{6708}	353·4	353·7	+0·3	,,

There was no change in rotation even after 3 hours.

TABLE XVI.

1:4-*Naphthylenebisaminomethylenecamphor in Pyridine.*

$$[\alpha] = \pm \frac{97{\cdot}40}{\lambda^2 - 0{\cdot}1606} \; ; \; \lambda_0 = 0{\cdot}4008.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line.	[α]calc. =C.	[α]obs. =O′.	O′−C.	Concn. g./100 c.c.
0·0804	+1·0°	+708·9°	Hg_{5461}	±707·9°	−708·1°	+0·2°	0·0812
,,	−1·7	559·7	Hg_{5780}	561·4	560·2	−1·2	,,
,,	±0	522·4	Na_{5893}	522·4	523·4	+1·0	,,
,,	+0·7	460·2	Li_{6104}	459·5	457·4	−2·1	0·0820
,,	+0·8	335·8	Li_{6708}	336·6	335·5	−1·1	,,

The solution did not undergo any mutarotation.

TABLE XVII.

1:4-*Naphthylenebisaminomethylenecamphor in Benzene.*

$$[\alpha] = \pm \frac{92{\cdot}47}{\lambda^2 - 0{\cdot}1584} \; ; \; \lambda_0 = 0{\cdot}3980.$$

Dextro					*Laevo*		
Concn. g./100 c.c.	O−C.	[α]obs. =O.	Line.	[α]calc. =C.	[α]obs. =O′.	O′−C.	Concn. g./100 c.c.
0·0816	+0·3°	+661·8°	Hg_{5461}	+661·5°	−662·5°	+1·0°	0·0800
,,	+0·6	527·0	Hg_{5780}	526·4	525·0	−1·4	,,
,,	+0·3	490·3	Na_{5893}	490·0	491·2	+1·2	0·0804
,,	−1·8	429·9	Li_{6104}	431·7	431·3	−0·4	0·0800
,,	+1·4	318·6	Li_{6708}	317·2	318·8	+1·6	,,

There was no change in rotation even after 24 hours.

We wish to make grateful acknowledgment to the Government of Bihar and Orissa in the Ministry of Education, for the grant of a research scholarship to one of us (B.B.) which has enabled him to take part in this investigation.

We also wish to acknowledge the valuable assistance which we received from Babu Indramani Mahanti, B.Sc., the Head Assistant of the Chemical Department.

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An Improved Method of Preparation of Substituted Amides and Hydrazides.

By Sohrab M. Mistry and Praphulla Chandra Guha.

Of all the methods available for the preparation of diaryl carbamides, those involving the use of urea and other derivatives of carbonic acid (*e.g.*, urethane, carbonic ester, phenylurea, phenylcarbonate, carbonyl chloride, etc.) are recommended since these can be easily procured and give satisfactory yields. (Hoffman and Steiner, *Annalen*, 1848, **70**, 138; Hentzschel, *J. pr. Chem.*, 1882, *ii*, **27**, 499; Claus, *Annalen*, 1875, **179**, 126; Wilm and Wischin, *Annalen*, 1868, **147**, 160; Bender, *Ber.*, 1880, **13**, 699; Eckenroth, *Ber.*, 1885, **18**, 516; Baeyer, *Annalen*, 1864, **131**, 252; Weith, *Ber.*, 1876, **9**, 821; Manuelli, Ricca-Rosellini, *Gazzetta*, 1890, **29**, II, 126; Frerichs, *Arch. Pharm.*, 1899, **237**, 316).

In connection with another piece of work, the preparation of *pp*-diacetaminodiphenylurea was attempted after the method of Schiff and Ostrogovitch (*Annalen*, 1896, **293**, 376) which consists in heating acetyl-*p*-phenylenediamine with urea, but most of the product was found to be insoluble in boiling hydrochloric acid. The substitution of phenyl carbonate or urethane (*cf.* Eckenroth; Manuelli and Ricca-Rosellini, *locc. cit.*) for urea gave no better result. The action of carbonyl chloride in toluene solution upon acetyl-*p*-phenylenediamine (*cf.* Hoffman; Hentzschel, *locc. cit.*) gave a dark coloured amorphous mass. In all these cases it was found very difficult to control the reaction and so the use of a liquid reaction medium was thought of and the action of urea upon acetyl-*p*-phenylenediamine was tried in boiling *iso*amyl alcohol. The beautifully crystalline product obtained in this reaction (m.p. 344°) could be completely hydrolysed with concentrated hydrochloric acid.

It was thought worth while to try the general applicability of this method in bringing about condensation between divers types of amines, diamines, hydrazines, thiosemicarbazides, etc., on the one hand and amides like urea, thiourea, oxamide, malonamide, succinamide, acetamide, benzamide, phthalamide on the other.

It can be seen from the results given in the experimental portion that, excepting aromatic-*o*-nitroamines and hydrazines and aminobenzenesulphonic acids which do not react at all, all the others give a fairly satisfactory yield of the substituted amides or hydrazides as the case may be. Aromatic acid amides do not react with aryl amines. In case of hydrazine hydrate and urea, whatever may be the quantity of the hydrate taken (one or two molecules), semicarbazide is always obtained to the complete exclusion of the equally expected carbohydrazide. The advantages offered by this method are that—

(*a*) the reactions are well controlled,

(*b*) the method gives good yield, and

(*c*) the products obtained by this method are generally pure and seldom require further purification.

Experimental.

The amide (1 mol.) and the amine or hydrazine (2 mols.) mixed with sufficient amyl alcohol are heated over a free flame under reflux, till the evolution of ammonia which is very profuse in the beginning becomes negligible. The product is purified by means of very dilute hydrochloric acid which dissolves away the unchanged base, as also most of the unreacted amide. Special methods of purification, analytical results of new compounds, and only the yield and melting point of known compounds are given. Substances No. 1—20 were obtained from an amine and urea.

1. Carbanilide from anilin (m.p. 238°; yield, 80%).

2. Di-*m*-tolylurea from *m*-toluidine (m.p. 232°; yield 70%). Cosack (*Ber.*, 1879, **12**, 1449) gave m.p. 217° while Gatterman and Cantzler (*Ber.*, 1888, **25**, 1089) gave m.p. 203°.

3. Di-*p*-tolylurea from *p*-toluidine (m.p. 262-63°; yield 80%).

4. *m*-Dinitrodiphenylurea from *m*-nitroaniline (yield, 70%). A pasty mass is obtained which is to be pressed on a Buchner funnel and dried in a desiccator.

5. *p*-Dinitrodiphenylurea from *p*-nitroaniline (m.p. 310°; yield, 90%).

6. Di-β-naphthylurea from β-naphthylamine (m.p. 309° decomp.; yield, 95%) (*cf.* Guha and Saletore, *J. Indian Chem. Soc.*, 1929, **6**, 574).

7. Di-α-naphthylurea from α-naphthylamin (m.p. 296° decomp.; yield, 95%). Guha and Saletore (*loc. cit.*) give the same m.p.

8. *pp*-Diacetylaminodiphenylurea from acetyl-*p*-phenylenediamine (m.p. 344°; yield, 85%).

9. Dibenzylurea from benzylamine (m.p. 167°; yield, 95%).

10. m-*Dihydroxydiphenylurea*, from *m*-aminophenol, crystallises from alcohol (m.p. 215° decomp.; yield, 80%). (Found: N, 12·16. $C_{13}H_{12}O_3N_2$ requires N, 12·3 per cent.).

11. p-*Dihyroxydiphenylurea*, from *p*-aminophenol, crystallises from alcohol (m.p. 288° decomp.; yield, 95%). (Found: N, 12·21. $C_{13}H_{12}O_3N_2$ requires N, 12·3 per cent.).

12. 2:4-Dihydroxytetrahydro-1:2:3:4-quinazoline from *o*-aminobenzoic acid (m.p. 353° decomp.; yield, 80%) (*cf. J. Amer. Chem. Soc.*, 1916, **38**, 1611; 1917, **39**, 2437).

13. *o*-Phenyleneurea from *o*-phenylenediamine (m.p. 311°; yield, 95%).

14. *m*-Phenyleneurea (polymerised product) from *m*-phenylenediaminehydrochloride (m.p. 310° decomp.; yield, 93%).

15. Diphenyleneurea from benzidine (sublimation and darkening at 300°; yield, 90%).

16. Semicarbazide from hydrazine hydrate (m.p. 97°; yield, 78%). Care should be taken in avoiding a large quantity of amyl alcohol. Addition of ethyl alcohol to the reaction mixture is useful.

17. Diphenylcarbohydrazide from phenylhydrazine (m.p. 167° after previous softening at 158°; yield, 95%).

18. pp-*Dinitrodiphenylcarbohydrazide*, from *p*-nitrophenylhydrazine formed yellow crystals from benzene or glacial acetic acid (m.p. 361°; yield 50%). (Found: N, 25·2. $C_{13}H_{12}O_5N_6$ requires N, 25·3 per cent.).

19. pp-*Dibromodiphenylcarbohydrazide*, from *p*-bromophenylhydrazine. Yellowish crystals from glacial acetic acid turn violet after sometime (m.p. 236° decomp.; yield, 85%). (Found: N, 13·9. $C_{13}H_{12}ON_4Br_2$ requires N, 14·0 per cent.).

20. (*a*) 1-Phenyl-2-phenylamino-5-thiol-1:3:4-triazole soluble in alkali (m.p. 210°);

(*b*) 2:5-Endoxy-1:3:4-triazole soluble in water (m.p. 250°);

(*c*) 2-Keto-5-phenylamino-2:3-dihydro-1:3:4-thiodiazole insoluble in water or alkali (m.p. 246°).

These three compounds were obtained from 4-phenylthiosemicarbazide (total yield, 60%), and were separated by the method of Guha and Sen (*J. Indian Chem. Soc.*, 1927, **4**, 43).

21. *p*-Monoacetylaminodiphenylurea from acetyl-*p*-phenylenediamine and phenylurea (m.p. 244° decomp.; yield, 95%).

22. *pp*-Diacetylaminodiphenylthiourea from acetyl-*p*-phenylenediamine and thiourea (m.p. 244° decomp.; yield, 50%).

23. Thiocarbanilide from aniline and thiourea (m.p. 152°; yield, 95%).

24. 4-Phenylthiosemicarbazide, instead of *pp*-diphenylthiocarbohydrazide as expected, from phenylhydrazine and thiourea (m.p. 198° decomp.; yield, 70%).

25. Oxanilide from aniline and oxamide (m.p. 252°; yield, 90%).

26. Oxalyldiphenylhydrazide from phenylhydrazine and oxamide (m.p. 274°; yield, 30%).

27. pp-*Diacetylaminodiphenyloxamide* from acetyl-*p*-phenylenediamine and oxamide (m.p. above 370°; yield, 60%). The method of purification is different from the general method. The compound being easily hydrolysable by hydrochloric acid, the reactants are dissolved away by means of warm dilute alcohol leaving behind the product. The dihydrochloride was prepared by evaporating the hydrolysed compound to dryness. The hydrochloride and the free base are colourless, crystalline compounds. (Found: N, 16·9. $C_{14}H_{16}O_2N_4Cl_2$ (dihydrochloride) requires N, 16·4 per cent).

28. Malonanilide from aniline and malonamide (m.p. 222°; yield, 95%).

29. Malonyldiphenylhydrazide from phenylhydrazine and malonamide (m.p. 194-95°; yield, 90%). Asher (*Ber.*, 1897, **30**, 1024) gave m.p. 184°. Freund and Goldschnidt (*Ber.*, 1888, **21**, 1241) gave m.p. 187°.

30. pp-*Diacetylaminodiphenylmalonamide* from acetyl-*p*-phenylenediamine and malonamide (m.p. 235° decomp.; yield, 60%). The same method of purification as for the corresponding oxamide compound (No. 27) was followed. It crystallises from 88 per cent

alcohol. (Found: N, 15·9. $C_{15}H_{18}O_2N_4Cl_2$ (dihydrochloride) requires N, 15·8 per cent.).

31. Succinanilide from aniline and succinamide (m.p. 228°: yield, 50%).

32. Succinyldiphenylhydrazide from phenylhydrazine and succinamide (m.p. 207-8°; yield, 30%). Fischer and Passmore (*Ber.*, 1889, **22**, 2734) gave m.p. 201° decomp.

33. pp-*Diacetylaminodiphenylsuccinamide* from acetyl-*p*-phenylenediamine and succinamide (m.p. 347° decomp., yield, 60%). The method of purification is similar to compounds No. 27 and No. 30. The colourless, crystalline base (m.p. 172°) obtained by hydrolysis was analysed. (Found: N, 19·8. $C_{16}H_{18}O_2N_4$ requires N, 20 per cent.).

34. Acetanilide from aniline and acetamide on complete removal of amyl alcohol and crystallisation of the residue from hot water (m.p. 114°; yield, 80%).

p-Aminobenzoic acid reacts with urea to give a 90 per cent. yield of a white amorphous compound (m.p. above 370°) which could not be purified further and gave varying results on analysis. The compound thus remains unidentified.

No definite compound could be isolated from the tarry mass formed in the reaction between acetamide and phenylhydrazine.

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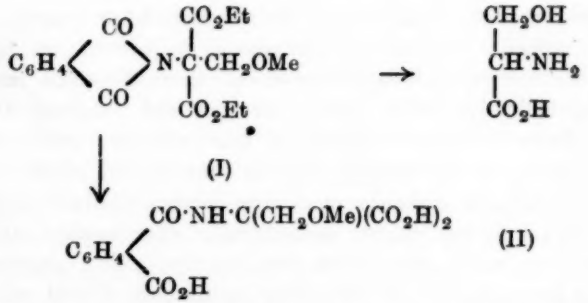
A New Synthesis of Serine.

By Susil Kumar Mitra.

Serine, α-amino-β-hydroxypropionic acid, has previously been synthesised by Erlenmeyer, jun., (*Ber.*, 1902, **35**, 3769), by Fischer and Leuchs (*Ber.*, 1902, **35**, 3787), and by Leuchs and Geiger (*Ber.*, 1906, **39**, 2644). The present paper describes another synthesis of serine by following Gabriel's method of synthesis of α-amino-acids.

The sodium salt of diethyl phthalimidomalonate was condensed with chloromethyl ether, the product being methoxymethylphthalimidomalonic ester (I).



Attempts to hydrolyse (I) to serine by heating with hydrochloric acid of varying strength or hydrobromic acid (*d* 1·8) in a sealed tube resulted in profound decomposition of the molecule, and phthalic acid and ammonium chloride (or bromide) were formed in quantity even at 100°, while no appreciable change was noticed on boiling the ester with 10 or 20 % hydrochloric acid for about 5 hours. The formation of the ammonium salt is probably due to the labile nature of the NH_2-group, attached to a reactive methylene group. Success was however attained by conducting the experiment with concentrated hydrobromic acid at 48°, when the primary product was found to be methoxymethylphthalimidomalonic acid. On heating above its melting point, this substance yielded an oil which was

converted into serine hydrochloride by heating with fuming hydrochloric acid in a sealed tube at 100°.

Methoxymethylphthalimidomalonic ester (I) gives considerable quantities of phthalic acid by hydrolysis with sodium hydroxide (*N* to 5*N*) between 50° and 100°. By conducting the hydrolysis in alcoholic potassium hydroxide solution, a potassium salt, $C_{13}H_{10}O_8NK_3$, presumably (II), was obtained. The acid was unstable. On treatment with hydrochloric acid, carbon dioxide was evolved and a viscous oil separated out. This oil on being boiled with concentrated hydrochloric acid gave serine hydrochloride.

Experimental.

Phthalimidomalonic Ester.—Sorensen's method (*Compt. rend.* 1903, **6**, 1) was modified as follows:

Potassium phthalimide and ethyl bromomalonate were heated for 2 hours under reflux in xylene solution. The filtrate, after separation of potassium bromide, was freed from xylene under reduced pressure, when, pure phthalimidomalonic ester (m. p. 73°) was obtained in an yield of 78 per cent.

Methoxymethylphthalimidomalonic Ester (I).—The interaction of phthalimidomalonic ester (20 g.) and sodium (1·6 g.), in ethereal solution, though at first vigorous, stops after a time owing to the formation of an incrustation of the resulting sodium salt. In presence of a little alcohol, the reaction proceeds smoothly. To the cooled sodium salt, chloromethyl ether (9 g in 20 c.c. ether) was added drop by drop. The reaction was complete in about 2 hours. The mixture was diluted with water, the ethereal layer separated, dried over ignited sodium sulphate and the ether removed, when the substance was left behind as silky needles (yield, 60%). It is soluble in benzene, xylene, ether, acetone and hot alcohol, and sparingly soluble in cold alcohol. It was crystallised from alcohol in white needles, m. p. 127°. (Found: C, 58·4; H, 5·4; N, 4·01. $C_{17}H_{19}O_7N$ requires C, 58·45; H, 5·44; N, 4·01 per cent.).

Methoxymethylphthalmidomalonic Acid.—The above ester (10 g.) and hydrobromic acid (50 c. c. *d* 1·8) were heated in a sealed tube at 48° for 2 hours, when the substance gradually went into solution, and ethyl bromide separated out as an oil. On opening the tube and keeping at 50-60° for some time to remove ethyl

bromide and hydrobromide acid fumes, the above acid separated out along with a little phthalic acid. This was quickly filtered off and the filtrate diluted to twice its volume with water and cooled in ice when the pure acid crystallised out (yield, 50%). It melts at 102°, and dissolves easily in ether and acetone but with difficulty in alcohol. It is sparingly soluble in water (hot or cold) and was separated from phthalic acid by digestion with hot water. On long standing in presence of concentrated acid, it suffered hydrolysis. At 140-145° it evolves carbon dioxide forming an oil. (Found: C, 54·2; H, 4·1; N, 4·65. $C_{13}H_{11}O_7N$ requires C, 53·24; H, 3·75; N, 4·77 per cent.).

The *silver salt* was prepared by adding silver nitrate to the aqueous potassium salt of the acid. The precipitate, a white granular powder, was washed with water and dried in an amber coloured desiccator. (Found: Ag, 32·3, $C_{13}H_9O_7NAg_2$ requires Ag, 42·6 per cent.).

Serine Hydrochloride.—Methoxymethylphthalimidomalonic acid (5 g.) was heated with fuming hydrochloric acid (15 c.c.) in a sealed tube on the water-bath for 9 hours. Phthalic acid was filtered off from the reaction products, the solution was extracted with ether and the aqueous portion was concentrated on a water-bath. The syrupy liquid deposits, on standing, crystals of serine hydrochloride (yield, 50%). (Found: C, 24·7; H, 5·9; N, 9·71. $C_3H_7O_3N$, HCl requires C, 25·4; H, 5·65; N, 9·9 per cent.).

Alkaline Hydrolysis of Methoxymethylphthalimidomalonic Ester.—To a saturated hot alcoholic solution of the ester (10 g.) was gradually added a hot saturated solution of potassium hydroxide in alcohol (6 g.). The yellow solution soon became colourless and a white precipitate began to come down. After refluxing for ½ hour the precipitate was collected, dissolved in the minimum quantity of water and reprecipitated by alcohol (yield, 80%). (Found: N, 3·33; K, 27·79. $C_{13}H_{10}O_8NK_3$ requires N, 3·29; K, 27·53 per cent.).

The above potassium salt was gradually treated with *N*/10-hydrochloric acid, till the solution was acid to congo-red. Carbon dioxide was profusely evolved and the solution was evaporated down on a water-bath when an oil was left behind. The oil was taken up with alcohol, the alcohol removed and the residual oil heated with four times its weight of fuming hydrochloric acid under reflux for 4 hours. Phthalic acid was then removed from the cooled reaction product, the solution was evaporated to dryness and the residue taken up

with a minimum quantity of water and filtered. The filtrate was again concentrated and allowed to stand when serine hydrochloride separated out (yield, 55%). (Found: C, 25·9; H, 5·7; N, 10·1. $C_3H_7O_3N,HCl$ requires C, 25·4; H, 5·65; N, 9·9 per cent.).

Serine.—Serine hydrochloride (5 g.) solution was vigorously agitated with freshly precipitated moist silver oxide (6 g.) for ½ minute and quickly filtered. The filtrate was digested with animal charcoal for 1 hour, filtered, the filtrate concentrated on water-bath, and the serine precipitated by alcohol. It was finally crystallised from water (yield, 90%). It shrinks at 208° and melts at 246° (decomp.). (Found: C, 34·5; H, 6·8; N, 13·26. $C_3H_7O_3N$ requires C, 34·28; H, 6·6; N, 13·3 per cent.).

The *phenyl cyanate* derivative melted at 159° (*cf.* Fischer and Leuchs, *loc. cit.*). (Found: N, 12·32. Calc. for $C_{10}H_{12}O_4N_2$ N, 12·5 per cent.).

In conclusion I wish to express my sincere thanks to Sir P. C. Rây for his kind interest in this investigation and for placing the resources of his research laboratory at my disposal.

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Experiments with Precipitated and Colloidal Manganese Dioxide.

By Jnanendranath Mukherjee, Satyaprasad Roy Choudhury and M. R. Subba Rao.

It has been suggested (Dhar, *J. Phys. Chem.*, 1927, **31**, 649, 997 and earlier papers) that on coagulation the electric charge of the coagulated particles is completely neutralised and that this changes their adsorbing properties (*ibid*, 1924, **28**, 465. See also Weiser, *ibid*, 1920, **24**, 30, 630). An attempt has also been made (Dhar, *loc. cit.*) to correlate (1) the influence of the dilution of a sol on the coagulating concentration of electrolytes, (2) ionic antagonism and (3) acclimatization through the adsorption of similarly charged ions by the colloidal particle and a 'normal' and an 'abnormal' dilution rule have been proposed as follows: 'Normally,' the greater the dilution of a sol, the less would be the amount of electrolyte necessary to coagulate it, provided that the relative adsorption of similarly charged ions by the sol does not increase on dilution. A higher coagulating concentration would be 'abnormal' and is to be attributed to the adsorption of similarly charged ions. These conceptions have been the subject of some criticism. (See Weiser, *loc. cit.*; *J. Phys. Chem.*, 1925, **29**, 962; Dhar's reply, *ibid*, 1926, **30**, 628; *J. Indian Chem. Soc.*, 1929, **6**, 17).

Recent cataphoretic measurements (Mukherjee and co-workers, *J. Indian Chem. Soc.*, 1928, **5**, 697, 735; *Nature*, 1928, **122**, 608; Kruyt and Willigen, *Kolloid Z.*, 1928, **44**, 22) establish, contrary to the assumptions referred to above, that coagulation takes place even when the colloidal particles carry considerable electrical charges and that it is not possible to speak of a critical potential (*Cf.* Powis).

Dhar and his co-workers (*loc. cit.*) have worked with both positive and negative manganese dioxide sols. In this paper the parallelism between 'abnormal' behaviour, adsorption of ions and ionic antagonism has been examined.

Experimental.

The 'negatively charged sols' were prepared according to Chakravarti and Dhar (*loc. cit.*). To a standard solution of potassium permanganate, hydrogen peroxide solution (Merck's 10 per cent. by vol.) was added at room temperature in small quantities with stirring until a test portion on coagulation with $BaCl_2$ left a colourless or slightly coloured upper layer.

The sol became unstable on dialysis in parchment paper bags, probably due to chemical reaction. The undialysed sols were stable for months and were used for experiments. The sol was treated with excess of standard oxalic acid (containing sulphuric acid), warmed to 60° and titrated against standard potassium permanganate solution. A and B contain respectively 0·443 g. and 0·610 g. of MnO_2 per litre. The total manganese in sol A determined by the phosphate method and calculated as MnO_2 was ·527 g. per litre. The particles carried a negative charge as measured by the method of moving boundaries.

The positively charged sols were prepared according to Ghosh and Dhar (*loc. cit.*). A standard solution of ferric chloride is mixed with a solution of potassium permanganate. Hydrogen peroxide is then added in small quantities at a time and stirred till there is hardly any excess of permanganate. The sol is then dialysed for about 10 days until free from iron and chlorine. These sols are very stable even after dialysis.

Composition.—The dioxide (I), the total manganese expressed as dioxide (II) and iron as ferric oxide (III) in grams per litre of sol were for these sols as follows:

Table I.

	I	II	III
A^+	0·00	0·05	4·251
B^+	0·10	0·10	2·024
C^+	0·29	1·92	2·724

The particles carried a positive charge.

Manganese dioxide Precipitates, A and B, were prepared respectively according to Ghosh (*J. Chem. Soc.*, 1926, **128**, 2605) and to Sarkar and Dhar (*Z. anorg. Chem.*, 1922, **121**, 135), washed free from

electrolytes and air-dried. 'A' contained 47·10 per cent. MnO_2 and 51·46 per cent. total manganese expressed as MnO_2. The particles were found to be negatively charged. 'B' (dried in a steam oven) contained 41·12 per cent. MnO_2 and 58·34 per cent. total manganese calculated as MnO_2. Endosmotic as also cataphoretic experiments with the sol formed by shaking the precipitates showed that the particles were negatively charged.

Equicoagulating concentrations were measured according to the procedure used before (*J. Chem. Soc.*, 1924, **125**, 794). Equicoagulating concentrations given below produced the same stage of coalescence in three minutes. For coagulation by a single electrolyte, a definite volume (5 c. c.) of the sol was taken in one tube and varying quantities of the electrolyte were taken in another tube together with sufficient amount of water to make the volume in the latter tube equal to 5 c. c. For dilutions 2·5 c. c. and 1·25 c. c. respectively of the sol were made up to 5 c. c. with water and electrolyte added as before.

For coagulation by a mixture of two electrolytes 5 c. c. of the sol were taken in one tube and in another an amount (insufficient for coagulation) of one electrolyte with varying amounts of the second and enough water to make the volume of the mixture (in the second tube) equal to 5 c. c.

Adsorption Experiments.

Precipitate.—A known weight of the precipitate was treated with 50 c.c. of the electrolyte in Jena glass bottles and after vigorous shaking the contents were left in contact for 24 hours. The supernatant liquid was then pipetted off and analysed for the concentration of the various ions. In some cases the p_H value of the liquid was determined and compared to that of the salt solutions used. The experiments were repeated with half and one-fourth amounts of the precipitate.

Sols.—20 C.c. were treated with 30 c. c. of the electrolyte. After shaking and leaving overnight the supernatant liquid was analysed. The experiments were repeated by taking 10 c. c. of the sol and adding 10 c. c. of water and 30 c. c. of the electrolyte.

Results and Discussion.

Adsorption Experiments.

TABLE II.

Sol B^-.

Conc. of sol.	Gram equivalent of electrolyte present per litre.	Amount adsorbed in g. equivalents of Cation	Amount adsorbed in g. equivalents of Anion.	Ratio of adsorption Anion/Cation.
20 C. c. sol	0·061*N*-$BaCl_2$	0·000582	0·000485	0·833
10 C. c. sol + 10 c. c. water	0·061 *N*-$BaCl_2$	0·000544	0·000454	0·8345
20 C c. sol	0·1176 *N*-$CuCl_2$	0·0015	0·00132	0·88
10 C. c. sol + 10 c. c. water	0·1176 *N*-$CuCl_2$	0·00136	0·00127	0·93

TABLE III.

Coagulating Concentrations.

Sol A^-.

Conc. of sol.	KCl.	$BaCl_2$.	$AlCl_2$.	$AlCl_2$.
1 : 1	0·051 *N*	0·00071 *N*	0·0021 *N**	0·0012 *N* (0·1050*N*)**
1 : 3	0·060 *N*	0·00049 *N*	0·0011 *N**	(0·1245 *N*)**
1 : 7	0·120 *N*	0·00021 *N*	0·00091 *N**	(0·2394 *N*)**

TABLE IV.

Ionic Antagonism.

Sol B^-.

% of KCl.	% of NaCl.	% of $BaCl_2$.	% of $AlCl_3$.
0	100 (·0292 *N*)†	100 (·00092 *N*)	100 (·0018*N*)
4·6	—	89·1	—
9·3	89·5	—	87·7
18·6	—	58·7	—
23·2	75·4	—	73·1
46·5	50·9	28·3	55·2
100	0	0	0
(·0398*N*)†			

* Another sample C_1^- for which the coagulating concentration of KCl was 0·066*N*.

** The second coagulating concentration presumably after reversal.

† NaCl has a greater coagulating power than KCl contrary to the observation of Ghosh and Dhar (*J. Phys. Chem.*, 1927, 31, 189), who however used a sol dialysed free from alkali. With another sol (undialysed), the following coagulating concentrations were observed : KCl, ·0363*N*; NaCl, ·084*N*.

TABLE V.

Ionic Antagonism.

Sol A^-.

% of KCl.	% of $BaCl_2$.	% of K_2SO_4.	% of K_3PO_4.	% of $K_4Fe(CN)_6$.
0	100 (·00071 *N*)	100 (·0432 *N*)	100 (·0954 *N*)	100 (·055 *N*)
9·1	66·2	—	—	—
18·2	53·5	75	85·3	56·7
36·4	28·2	54·2	66·7	23·3
54·5	—	29·2	42·1	—
100 (·0509 *N*)	0	0	0	0

Aluminium has a weaker coagulating power than barium. Ghosh and Dhar (*loc. cit.*) observed the same thing. On dilution the sol behaves like arsenious sulphide, being stabilised against potassium ions and sensitised against barium and aluminium (first coagulation), contrary to Dhar and Ghosh, who observed uniform sensitisation on dilution. Evidently the present sol, though prepared in the same manner, indicates an 'abnormal' behaviour. It should therefore show 'ionic antagonism' as both are stated by Dhar to be correlated through a common cause, namely, a strong preferential adsorption of similarly charged ions. Tables IV and V signify however that the expected ionic antagonism is completely absent. Ghosh and Dhar also did not observe any ionic antagonism with their sol nor observe a higher coagulating concentration of potassium chloride. The so-called normal or abnormal behaviour thus depends on the particular preparation even if the same method be adopted.

Table II (as also the results of Dhar and co-workers) shows that cations are adsorbed more strongly than anions. We think however that on dilution, the ratio of their adsorption (probably) remains constant within the limits of error. Dhar ascribes the sensitisation to a relatively greater adsorption of the oppositely charged ion as a result of the dilution and stabilisation to that of the similarly charged ion. It is not obvious why dilution as such must have this effect. Assuming an equilibrium and that the properties of the particles do not change on dilution (see later), a greater adsorption will be observed only when the amounts adsorbed are great compared to the

total amount present, so that the equilibrium concentration increases. But this need not necessarily change either the amount adsorbed, if the concentration is high, or the ratio of their adsorptions in the manner assumed by Dhar.

The coagulation with aluminium (Table II) shows in the first zone of precipitation a 'normal' and in the second an 'abnormal behaviour, which is to be interpreted as showing that the ratio of its adsorption to that of chlorine increases throughout the range of concentrations. As the particles are negatively charged in the first zone and positively in the second, we have sensitisation in the one case and stabilisation in the other. The ratio of adsorption should however tend to a constant value, as the concentration increases; but, the rapid increase in the coagulating concentration, in the second zone, points to the contrary. Further different types of curves are met with in adsorption phenomena indicating that the ratio of adsorption may show a very complicated behaviour on dilution.

There are other more serious objections against the simple explanation of Dhar. It ignores the actual effects of dilution. Recent work (Mukherjee and co-workers, *loc. cit.*, also results communicated for publication) shows that, though on dilution the sol becomes sensitised, the cataphoretic speeds of particles of ferric hydroxide sols show a *decrease or an increase*, depending on the preparation and the degree of dilution. A detailed consideration of the large number of factors concerned thus appears to be required. Moreover, estimation of amounts of ions adsorbed cannot give a definite idea as to their effect on the stability. Thus an oppositely charged ion may be associated with a colloidal particle either in a 'free' (mobile) or in a ' fixed ' (on the solid side of the interface) state. When such an ion passes from the 'free' to the 'fixed' state or *vice versa*, chemical analysis cannot possibly indicate the difference, though it will have an obvious effect on the stability. Discussions as to the effect of relative changes in adsorption of the cation and anion, deduced from chemical analysis, are therefore futile and misleading. Similarly the distinction between adsorption by charged and neutral particles, that is supposed to be different and to occur as independent processes before and after coagulation, has no justification in fact, as coagulation seldom takes place at the isoelectric point.

The relative adsorptions of copper and chlorine ions also go against the above rule, as Dhar and Ghosh observed a normal behaviour with negative sols. The ratio anion to cation should decrease

instead of the slight increase observed in Table II. Lastly on account of the small quantities adsorbed, it is not desirable to place too much stress on the values of these ratios.

TABLE VI.

Adsorption.

Sol C^+.

Conc. of sol.	G. equivalent of electrolyte present per litre.	Amount absorbed in g. equivalent of Cation	Amount absorbed in g. equivalent of Anion.	Ratio of adsorption Cation/Anion.
20 C.c. of sol	0·592 *N*-$CuCl_2$	·00053	·000†	—
10 C.c. of sol + 10 c.c. of water	0·592 *N*-$CuCl_2$	·0011	·000†	—
20 C.c. of sol	0·54 *N*-$BaCl_2$	·00034	·00026	1·30
10 C.c. of sol + 10 c.c. of water	0·54 *N*-$BaCl_2$	·00028	·00020	1·40

TABLE VII.

Sol A^+.

Coagulating Concentrations in Normality

Conc. of sol.	KCl.	KNO_3*.	K_2SO_4.	$K_2C_2O_4$.	K_3PO_4.	$K_4Fe(CN)_6$.
1 : 1	·0092	·0952	·000456	·000452	·000595	·000061
1 : 3	·0111	·1130	·000288	·000288	·000268	·000041
1 : 7	·0134	·1250	·000205	·000205	·000189	·000052

TABLE VIII.

Ionic Antagonism.

Sol C^+.

% of KCl.	% of KNO_3.	% of K_2SO_4.	% of K_3PO_4.	% of $K_4Fe(CN)_6$.
0	100 (·0952 *N*)	100 (·00123 *N*)	100 (·00123 *N*)	100 (·00024 *N*)
5·55	93·75	—	71·8	73·8
8·33	—	74·1	—	—
19·44	68·75	55·55	38·5	52·3
41·65	50·00	33·33	20·55	28·6
100 (·0666 *N*)	0	0	0	0

* The coagulating concentrations of KNO_3 are for another sample. For this sample the coagulating concentration of KCl was 0·066 *N*.

† Adsorption within experimental error.

TABLE IX.

Ionic Antagonism.

Sol B^+. % of KCl.	% of K_2SO_4.	% of NaCl.	% of $MgCl_2$.
0	100 (·00045 *N*)	100 (·0184 *N*)	100 (·0177 *N*)
5	95	1·7	103
10	80	—	—
20	70	80·5	85·3
40	45	55·5	—
50	—	—	56
60	—	41	—
100 (·0185 *N*)	0	0	0

TABLE X.

Ionic Antagonism.

Sol B^+. % of K_2SO_4.	% of Na_2SO_4.	% of $MgSO_4$.
0	100 (·0005 *N*)	100 (·00051 *N*)
10	90	92·3
30	70	70
50	50	54
100 (·00045 *N*)	0	0

Sol A^+ obeys Schultze-Hardy law (Table VII) and the coagulating concentrations are in the order.—$NO_3 > Cl > SO_4$, C_2O_4, $PO_4 > Fe(CN)_6$. On dilution it behaves like the negative sol (of course against anions). Here also the observations of Dhar and his coworkers with the chloride and the nitrate (*J. Phys. Chem.*, 1927, **31**, 192) are contrary to ours, as they observed a normal behaviour; ionic antagonism is again absent with these two electrolytes though expected.

With barium chloride, the ratio of the adsorption of cation to anion does not change on dilution ; the amounts after adsorption were respectively barium, 1·8314 and 1·8355 and chlorine ·9493 and ·9512. The difference in the ratio is to be ascribed to the manner of estimating the adsorption by the very small differences in the concentrations. In the case of cupric chloride, copper appears to be

adsorbed but not chlorine ion. The observations in the previous section apply equally.

TABLE XI.

Adsorption Experiments.

Precipitate A.

Amount in g.	G. equivalents of electrolyte per litre.	Amount adsorbed in g. equivalents of :		Ratio of adsorption
		Cation.	Anion.	Cation/Anion.
2·4808	·1014 $BaCl_2$	·00127	·00103	1·23
4·1773	·1014 $BaCl_2$	·00127	·00104	1·22
2·0059	·153 $CuCl_2$	·000044	·00055	·08
4·5842	·153 $CuCl_2$	·00047	·00555	·085

We again find that the ratio remains practically constant. Dhar and his co-workers, however, found that the ratio, cation to anion, increases as the quantity of the adsorbent decreases.

TABLE XII.

Adsorption Experiments.

Precipitate B.

Amount of ppt. taken in g.	G. equivalent of electrolyte per litre.	Amount adsorbed in g. equivalents of :		Ratio of adsorption
		Cation.	Anion.	Cation/Anion.
·5788	·1014 $BaCl_2$	·0012	·00064	1·875
1·0112	·1014 $BaCl_2$	·0014	·00093	1·505
·5354	·196 $CuCl_2$	·0024	·00213	1·126
·9908	·196 $CuCl_2$	·00285	·00219	1·301
1·8691	·196 $CuCl_2$	·0036	·00213	1·690

The copper is adsorbed more than chlorine (Table XII) but the *ratio decreases* with a diminution in the amount and contrary to the observations of Dhar and his co-workers of *an increase*, which is in support of their hypothesis. Precipitates A and B are negatively charged. Dhar does not distinguish between adsorption by the ' positive ' sol (containing iron) and by the ' negative ' precipitates, as they account for the stabilisation of the former against copper chloride on the basis of the adsorption of the latter. This is also in contrast with the distinction between neutral and charged particles. It appears from the data given below that the relative adsorption in the case of the positive sol depends on the sample (probably on the iron content):

TABLE XIII.

Positive Sol: Electrolyte – $CuCl_2$.

Our Observation: Vol. sol A (c. c.).	Conc. (normal).	Iron content g. of Fe_2O_3 per litre of sol.	Ratio of adsorption. Cation/Anion.
20	·592	2·724	$\frac{\cdot 00053^*}{0}$
10	,,	,,	$\frac{\cdot 0011^*}{0}$
(Dhar, *J. Phys. Chem.*, 1927, **31**, 1029, 1930).			
20	·01	Not given	10·7
10	,,	,,	9·1

Dhar and Sarkar (*loc. cit.*) have pointed out the formation of manganates by the interaction of neutral electrolytes and potassium permanganates. This reaction and the stability of the manganates will depend on the hydrogen-ion concentration among other things. In the positively charged sol we have used, the amount of iron is considerable in comparison with the manganese content. The question arises whether we are to consider it as a sol of manganese dioxide or ferric manganate or a complex solid containing different solid phases, whose constitution can only be determined by separate

* The ratio of adsorption of cation to anion in this case bears no significance.

investigations. The positive sol adsorbs scarcely any chlorine but copper relatively strongly. The p^H of the supernatant liquid after coagulation of the positive sol is about 6·1 for barium chloride. The liberation of the chlorine at higher concentration is also not ruled out. It may not thus be profitable to discuss the results on the basis, that we are dealing with the same chemical substance in both sols (positive and negative—see also difference in composition of the precipitate) and that chemical reactions, changing the composition of the colloid (either *en masse* or of several layers of molecules on the surface) are ruled out.

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β-Diketones in Ring Formation. Part II.

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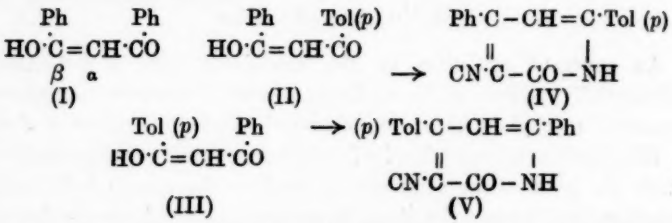
An apparent exception to the hypothesis that a β-diketone preferentially reacts in its enolic form with a substance containing a reactive methylene group was observed in the course of a study of the reaction between benzoylacetophenone and cyanoacetamide where the yield of the condensation product, 3-cyano-4 : 6-diphenyl-2-pyridone was found to be about 45 per cent. although the β-diketone is supposed to exist to the extent of 96 per cent. in the enolic form. (Basu, *J. Indian Chem. Soc.*, 1930, **7**, 481). With a view to establish the validity of the above statement and to examine the influence, if any, of the adjacent substituent groups in the enolic ketone on the course of such reactions, the present investigation was undertaken. It has been observed that this anomaly could be best explained on steric considerations; a fuller detail and explanation of this statement has been embodied in the course of the present work.

Cyanoacetamide has been condensed with (1) benzoyl acetophenone, (2) benzoyl-*p*-methylacetophenone and (3) dipropionyl methane, $Et{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}Et$. It has been noticed that the condensation with benzoylacetophenone in presence of sodium ethoxide (Michael's way) gives an yield varying between 5 and 20 per cent. dependent on the conditions of the reaction. But by conducting the reaction with diethylamine (Knoevenagel's way) a better yield is obtained in the course of 3 days. The yield further increases to more than 70 per cent. when the concentration of the cyanoacetamide is increased. The rise of temperature again has an adverse effect on the yield. The condensation product, 3-cyano-4 : 6-diphenyl-2-pyridone may also be obtained in about 75 per cent. yield by condensing α-ethoxy-ω-benzoylstyrolene, $Ph{\cdot}C(OEt)=CH{\cdot}COPh$, an O-ether of benzoylacetophenone. The reason for the low yield in the former case may be attributed to the inhibiting effect of the β-phenyl group in the unsaturated ketone (I) (*cf.* Ingold and Powell, *J. Chem. Soc.*, 1921, **119**, 1976) and the difference in that again when sodium ethoxide or diethylamine is used as the condensing agent may be due to the greater reversibility of the Michael reaction when sodium ethoxide is used as observed by Ingold and Perren (*J. Chem. Soc.*, 1922, **121**, 1416; *cf.* also Ingold, Perren and Thorpe,

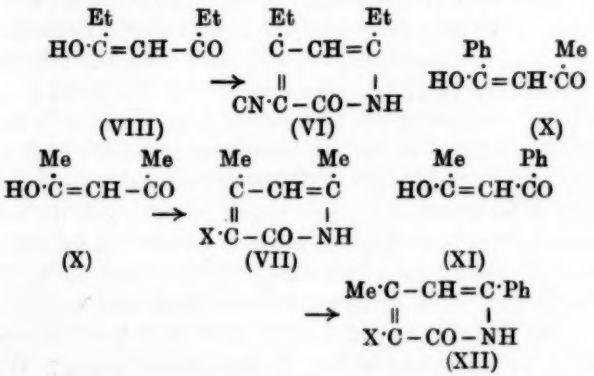
ibid, 1770) who found that the condensation which takes place in the presence of piperidine (or diethylamine) is reversed to some extent by sodium ethoxide, particularly in the case where the retrograde reaction is more pronounced.



The β-diketone, benzoyl-*p*-methylacetophenone may exist in the two enolic forms (II) and (III) and may evidently give rise to two different condensation products (IV) and (V). Condensing the diketone with cyanoacetamide in presence of diethylamine, a product melting indifferently between 245 and 280° (evidently a mixture) was isolated during the course of a week. On fractional crystallisation from acetic acid the main crop (66 per cent.), 3-cyano-4-phenyl-6-*p*-tolyl-2-pyridone (IV), m. p. 266-267° separated out. Its constitution was ascertained by direct comparison with a known specimen of the substance (Barat, *J. Indian Chem. Soc.*, 1930, **7**, 335). This on hydrolysis with 80 per cent. sulphuric acid gave 4-phenyl-6-*p*-tolyl-2-pyridone, m. p. 226-28°. The other crop of the condensation product, 3-cyano-6-phenyl-4-*p*-tolyl-2-pyridone (V), m. p. 311-12°, on hydrolysis gave 6-phenyl-4-*p*-tolyl-2-pyridone, m. p. 237-239°. In this case the total yield was found to be still lower as expected and even in the condensation product the main crop was derived from the enol (II) evidently due to the greater inhibiting effect of β-*p*-tolyl group as present in (III), on such condensation. That the reaction had taken place through the enolic phase was evident by the isolation of only 3-cyano-4-phenyl-6-*p*-tolyl-2-pyridone from the condensation product of cyanoacetamide with α-methoxy-ω-*p*-tolyl styrolene, $Ph{\cdot}C(OMe)=CH{\cdot}CO{\cdot}C_6H_4Me$ an O-ether of the β-diketone. Here also using one and half times the theoretical quantity of cyanoacetamide a better yield of the condensation product, calculated on the diketone employed was obtained.

The condensation product 3-cyano-4: 6-diethyl-2-pyridone (VI), from dipropionylmethane under the conditions described later, crystallised out from the reaction mixture after 3 hours and the total yield was 90 per cent. of the theory. But acetylacetone under

similar conditions affords 3-cyano-ψ-lutidostyril (VII, X=CN) within two to three minutes and the yield is almost quantitative. This difference between the two cases may also be accounted for by the effect of the heavier substituent (ethyl) in the enolic ketone (VIII) than the methyl in the analogous ketone (IX). On this consideration the action of cyanoacetamide on benzoylacetone is interesting to note. The β-diketone may exist in the two enolic forms (X) and (XI) the former predominating over the other according to Scheiber and Herold (*Annalen*, 1914, **405**, 295) but in its condensation the main product is 3-cyano-4-methyl-6-phenyl-2-pyridone (XII, X=CN) (Basu, *loc. cit.*) indicating a greater activity of the latter enol towards cyanoacetamide. This is in agreement with the former conclusion that a heavier group (phenyl) in the enol (X) inhibits the reaction and the reason for the occurrence of (XII) is that as the condensation proceeds and as the latter enol readily reacts, more of it is formed from the other with which it is in dynamic equilibrium and consequently the main product of the reaction is derived from the enol which is supposed to be originally present in the system in small quantity. All these are in complete agreement with the view expressed by Ingold, Perrin and Thorpe, (*loc. cit.*) that in Michael's reaction " the presence of a β-substituent considerably reduces the tendency towards condensation. The effect is a spatial one, the larger the group, the stronger is the inhibition. " Further work to study the effect of other substituent is in progress.



Considering certain conditions which govern the occurrence of a Michael reaction between a β-diketone and cyanoacetamide, it is also of interest to have an idea of the part taken by the methylene group of the cyanoacetamide molecule in all such condensations. So it

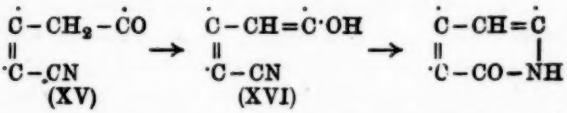
was found necessary to study the influence exerted individually by the substituents of the methylene carbon atom of the acetic ester residue (XIII).

Accordingly malonamide, $CH_2(CONH_2)_2$, was condensed with acetylacetone in the usual way when the known 4 : 6-dimethyl-2-pyridone-3-carbonamide (VII, $X=CONH_2$) separated after 3 days, the total yield being about 60 per cent. The compound was first synthesised by Knoevenagel and Cremer (*Ber.*, 1902, **35**, 239) from malonamide and aminoacetylacetone. Again the activity of ethyl cyanoacetate in such condensations has already been studied by Simonsen and Naik (*J. Chem. Soc.*, 1915, **107**, 793) who by condensing acetylacetone and ethyl cyanoacetate (piperidine) isolated mainly ethyl 4 : 6-dimethyl-2-pyridone-3-carboxylate (VII, $X=CO_2Et$) in 44 per cent. yield after several hours' heating. Benzoylacetone when similarly treated with ethyl cyanoacetate gave a crystalline substance, m.p. 216-17° which on hydrolysis with 80 per cent. sulphuric acid afforded the known 4-methyl-6-phenyl-2-pyridone (XIV), m.p. 180-81°. (Bardhan, *J. Chem. Soc.*, 1929, p. 2223) and evidently the crystalline substance must have been ethyl 4-methyl-6-phenyl-2-pyridone-3-carboxylate (XII, $X=CO_2Et$).

$CN\cdot CH\cdot COOEt$ (XIII)

$Me\cdot C-CH=C\cdot Ph$ (XIV)
$\quad\quad\quad

by Simonsen and Naik (*loc. cit.*) and it may be said that the cyano- and the carbonyl-groups in (XV) have undergone the intramolecular change through the intermediate formation of an enol (XVI).



(XV) (XVI)

When one of the above negative groups is substituted by phenyl or chlorine, (as in phenylacetonitrile, phenylacetamide or chloroacetamide) acetylacetone could not be induced to react with any of them under the usual conditions. Even on keeping the reaction mixture for 3—4 weeks and then heating it the amides could be recovered unchanged. Thus the evidence obtained from these observations indicates that the cyano-group is by far the more effective than any other group and that the reactivity of the methylene carbon atom depends on the total negative character of both the substituents and that if this does not reach a certain limit, the reactivity of the methylene group vanishes at least with respect to β-diketones.

Experimental.

1. *Benzoylacetophenone and Cyanoacetamide: Formation of 3-Cyano-4: 6-diphenyl-2-pyridone.*

The β-diketone was prepared by the method described in " Organic Syntheses ", Vol. VIII, p. 60; yield 60% ; m.p. 77-78° on crystallisation from 95 per cent. alcohol.

(*i*) *By Michael's method.*—An alcoholic solution of benzoylacetophenone (11·2 g.) was added to the suspension of sodiocyanoacetamide prepared by adding an alcoholic solution of cyanoacetamide (4·2 g.) to the required quantity of sodium also dissolved in alcohol. At once a deep yellow coloured solution was obtained and the crystalline sodium salt that separated out was left overnight at the room temperature. Next day water was added to make a clear solution, which on acidification gave a crystalline precipitate. This was filtered, well washed with alcohol and ether when 3-cyano-4: 6-diphenyl-2-pyridone, m.p. 320° (Basu, *loc. cit.*) was obtained only in 5% yield. From the washed liquor benzoylacetophenone was recovered unchanged. Conducting the reaction at 60° for 24 hours, so that the sodium salt of the β-diketone remains in solution, a somewhat better yield (18-20%) may be obtained but the β-diketone

at the same time undergoes partial hydrolysis to its components, as smell of ethyl benzoate is distinctly perceived in the washed liquor.

(*ii*) *By Knoevenagel's method.*—This has been already studied (Basu, *loc. cit.*) but in the present case the reaction at the room temperature (32-33°) is described. To an alcoholic solution of molecular quantities of benzoylacetophenone and cyanoacetamide a few c.c. of diethylamine was added. After 2 days, the shining crystals that had separated out was filtered off and the mother-liquor with the addition of a few more drops of diethylamine was again left overnight. Next day another crop separated when the solution was acidified. The total solid (yield, 65%) was filtered, washed well with alcohol and ether. Using one and half times the theoretical quantity of cyanoacetamide, the yield was 55 per cent. (calculated on the diketone employed) when the reaction was conducted at 100° for 6 to 8 hours and to more than 70 per cent. when conducted at the room temperature for more than 3 days.

(*iii*) *From O-Ether of Dibenzoylmethane.*—α-Ethoxy-ω-benzoylstyrolene, $Ph{\cdot}C(OEt){=}CH{\cdot}CO{\cdot}Ph$, was prepared according to Ruhemann and Watson (*J. Chem. Soc.*, 1904, **85**, 462) and obtained as an yellow oil, b.p. 214-15°/14 mm. An alcoholic solution of the ether (8·4 g.) was gradually added with shaking to a suspension of sodiocyanoacetamide prepared from cyanoacetamide (2·8 g.) in hot alcohol and sodium (0·77 g.) also dissolved in absolute alcohol. The colour of the mixture turned brown and it was left overnight. After 3 days, water was added, the sodium salt was decomposed by dilute hydrochloric acid and the product was filtered, well washed with alcohol and ether when 3-cyano-4: 6-diphenyl-2-pyridone, (m.p. 320°, 7 g.) was obtained. (Found: N, 10·15. $C_{18}H_{12}ON_2$ requires N, 10·3 per cent.).

2-*Benzoyl*-p-*methylacetophenone and Cyanoacetamide. Formation of* 3-*Cyano*-4-*phenyl*-6-p-*tolyl*-2-*pyridone* (IV) *and* 3-*Cyano*-6-*phenyl*-4-p-*tolyl*-2-*pyridone* (V).

(*i*) The β-diketone was prepared from benzal-*p*-methylacetophenone (Weygand, *Annalen*, 1927, **459**, 113) and was obtained in light yellow crystals, m.p. 84-85°. The condensation was effected as usual by means of diethylamine at the ordinary temperature. The crystals which separated after 4 or 5 days were collected and washed with a little alcohol. A further quantity of diethylamine was added to the mother-liquor, and left overnight. The crystal separated was again collected and washed with a little alcohol. The operation was

repeated till no more crystals separated out and finally the mother-liquor was concentrated and acidified with dilute hydrochloric acid. The precipitate was filtered, washed with alcohol and ether to remove the unchanged β-diketone. The time required for the whole operation varied from 7 to 10 days and the total yield was about 30 per cent. The crystallised product was generally found to melt between 250° and 260° and the product from the mother-liquor between 240° and 280°. Evidently the condensation product consisted of a mixture of the isomeric pyridone derivatives which were separated by fractional crystallisation from acetic acid in which the solubility of the two was found to be almost equal. The main product (about 66%) melted at 267° on recrystallisation from glacial acetic acid. It was 3-cyano-4-phenyl-6-*p*-tolyl-2-pyridone as proved by direct comparison with a sample prepared by Barat (*loc. cit.*). (Found: N, 9·8. $C_{19}H_{14}ON_2$ requires N, 9·79 per cent.). The pyridone derivative was difficultly soluble in alcohol but readily in pyridine from which it separated in fine prismatic needles. It is also soluble in concentrated sulphuric acid and forms a salt with alkali. On gently heating the substance with sulphuric acid (80%), till the evolution of carbon dioxide ceased, and pouring the acid solution on ice water 4-phenyl-6-*p*-tolyl 2-pyridone was obtained. On crystallisation from dilute alcohol it melted at 226-28°. (Found: N, 5·4. $C_{18}H_{15}ON$ requires N, 5·36 per cent.). It is also soluble in alkali and imparts a brown colouration to alcoholic ferric chloride.

After fractional crystallisation another crop, m.p. 311-12°, was isolated. It is moderately soluble in alcohol and more so in pyridine and dissolves in concentrated sulphuric acid but is precipitated unchanged on dilution with water, and forms a sodium salt when dissolved in warm sodium hydroxide. (Found: N, 9·7. $C_{19}H_{14}ON_2$ requires N, 9·79 per cent.). Most probably this is 3-cyano-4-*p*-tolyl-6-phenyl-2-pyridone. A mixture of this and its isomer (m.p. 267°) in equal proportion melted at 240-42°. The pyridone derivative on hydrolysis in the usual way afforded 4-*p*-tolyl-6-phenyl-2-pyridone which on crystallisation from dilute alcohol melted at 237-39°. (Found: N, 5·34. $C_{18}H_{15}ON$ requires N, 5·36 per cent.). Its alcoholic solution imparted a brown colouration to ferric chloride. Conducting the above reaction with an excess of cyanoacetamide, as in the previous case, an yield of about 52% was obtained.

(ii) *Condensation with O-Ether of Benzoyl-p-methylacetophenone.* —α-Methoxy-ω-*p*-tolylstyrolene, $Ph{\cdot}C(OMe)=CH{\cdot}CO{\cdot}C_6H_4{\cdot}Me$ (*p*),

was prepared according to Weygand's method (*loc. cit.*) and obtained as a thick yellow oil, b. p. 221-223°/22 mm. Its condensation with cyanoacetamide was effected exactly in the same way as in the case of the previous ether. The solid isolated, on crystallisation from aqueous pyridine melted at 267-68°, not depressed by admixing with the compound, m.p. 267°, previously described and was evidently 3-cyano-4-phenyl-6-*p*-tolyl-2-pyridone. (Found: N, 9·61. $C_{19}H_{14}ON_2$ requires N, 9·79 per cent.). On hydrolysis with sulphuric acid (80%) it also gave 4-phenyl-6-*p*-tolyl-2-pyridone.

Dipropionylmethane and Cyanoacetamide: *Formation of 3-Cyano-4:6-diethyl-2-pyridone* (VI).—The β-diketone was prepared from methyl ethyl ketone and ethyl propionate by the method of Fischer and Bartholomäus (*Ber.*, 1912, **45**, 1979) and obtained as a colourless liquid of agreeable odour, b. p. 175-77°/754 mm.

Cyanoacetamide (4·2 g.) was dissolved in water by warming and dipropionylmethane (6·4 g.) was added with just enough alcohol to effect the solution. About 2 c.c. of diethylamine being added, the yellow solution was warmed up to 50° and kept at that temperature for more than 2 hours. The flask was then removed and left at the ordinary temperature when crystals began to separate and soon a sludge was obtained. This (5 g.) was filtered off after half an hour and the mother-liquor with the further addition of diethylamine (1 c. c.) was left overnight. Next morning it was concentrated and then acidified with dilute hydrochloric acid when a further crop (3 g.) was obtained (total yield, 90%). On crystallisation from rectified spirit it melts at 186°. (Found: N, 15·5. $C_{10}H_{12}ON_2$ requires N, 15·9 per cent.). It is easily soluble in alcohol, chloroform, acetone, benzene and moderately in warm water. It readily dissolves in alkali from which it is obtained unchanged on acidification. Concentrated sulphuric or hydrochloric acid dissolves it and from the acid solution it may be recovered on dilution with water.

Hydrolysis: *Formation of 4:6-Diethyl-2-pyridone*.—The condensation product (1·5 g.) was heated with concentrated hydrochloric acid (10 c.c.) at 150° for 3 hours. Excess of the acid being removed on the water-bath, the residue was dissolved in minimum quantity of water, filtered and the filtrate on neutralisation with solid sodium carbonate gave the pyridone in almost quantitative yield. Crystallising from water it was obtained in small needles, m. p. 61-62°. (Found: N, 9·9. $C_9H_{13}ON$ requires N, 9·3 per cent.). This is soluble in almost all common organic solvents and also in alkali and

dilute acid. The alcoholic solution of the substance imparts a brown-red colouration to ferric chloride.

Acetylacetone and Malonamide: *Formation of* 4:6-*Dimethyl*-2-*pyridone*-3-*carbonamide* (VII, X=$CONH_2$). The amide was prepared by shaking ethyl malonate with a concentrated solution of ammonia. Its condensation with acetylacetone was effected just as in the previous case using malonamide in place of cyanoacetamide. The known product 4:6-dimethyl-2-pyridone-3-carbonamide (Knoevenagel and Cremer, *loc. cit.*) separated out in the form of a crystalline sludge after about 3 days. A further quantity was isolated after keeping the mixture again for a day with the addition of a few more drops of diethylamine and after the acidification of the final mother-liquor (total yield, 60 per cent.). It crystallises from boiling water with a molecule of water of crystallisation, m.p. 224-25°. (Found: N, 15·1. $C_{18}H_{10}O_2N_2,H_2O$ requires N, 15·2 per cent.). The compound on hydrolysis with concentrated hydrochloric acid gave a good yield of ψ-lutidostyril, m.p. 179-80°.

Acetylacetone and Chloroacetamide or Phenylacetamide.—A similar dilute alcoholic solution of chloroacetamide or phenylacetamide and acetylacetone in molecular quantities in presence of diethylamine did not afford any condensation product even after 3 or 4 weeks. On refluxing the mixture for 6 hours and evaporating the alcohol the amide was recovered unchanged. An attempt to condense phenylacetonitrile with acetylacetone according to the method of Simonsen and Naik (*loc. cit.*) met with no success.

Acetylacetone and Malononitrile.—The nitrile was obtained from cyanoacetamide according to Hesse's method (*Amer. Chem. J.*, 1896, **18**, 726) as a colourless liquid, b.p. 219-20°. A mixture of acetylacetone (5 g.) and malononitrile (3·3 g.) was cooled in ice and to it about 10 drops of diethylamine were slowly added. The solution at once turned red and became distinctly warmer when a yellow crystalline solid separated out. The flask was left in a refrigerator. Next morning the solid (5·5 g.) was filtered off and washed with a little cold alcohol. From the mother-liquor on acidification a trace (0·2 g.) of the product was isolated (yield, 77 per cent.).

On crystallisation from boiling water (charcoal) it melted at 289°, and was found to be 3-cyano-ψ-lutidostyril (VII, X=CN) by direct comparison and from mixed melting point determination.

Benzoylacetone and Ethyl Cyanoacetate: *Formation of Ethyl* 4-*Methyl*-6-*phenyl*-2 *pyridone*-3-*carboxylate* (XII, X=CO_2Et). An

equimolecular mixture of benzoylacetone and ethyl cyanoacetate after about 12 hours' heating with a few c.c. of diethylamine under reflux on a water-bath gave rise to a light yellow crystalline solid in a very low yield which could not be increased on further heating. Crystallising from glacial acetic acid it melted at 216-17° (decomp.). (Found: N, 5·9. $C_{15}H_{15}O_3N$ requires N, 5·5 per cent.). It is difficultly soluble in alcohol and dissolves in hot caustic soda solution. Its constitution was ascertained by its hydrolysis to the known 4-methyl-6-phenyl-2-pyridone (Bardhan, *loc. cit.*). The compound was heated with sulphuric acid (80%) for half an hour; the acid solution was poured over ice water, filtered and the filtrate was almost neutralised with sodium carbonate, and the solid on crystallisation from dilute alcohol melted at 180-81°. (Found: N, 7·6. $C_{12}H_{11}ON$ requires N, 7·8 per cent.). Evidently the condensation product is ethyl 4-methyl-6-phenyl-2-pyridone-3-carboxylate (XII, X=CO_2Et).

Benzoylacetone and Malononitrile.—To a cooled alcoholic solution of benzoylacetone (8·1 g.) and malononitrile (3·3 g.) diethylamine (1 c.c.) was added when the solution became dark red and warm. Within 15-20 minutes yellow crystals began to separate when the flask was left overnight in a refrigerator. Next day the crystals (6·6 g.) were collected and washed with little alcohol and ether; m.p. 306°. To the filtrate a few more drops of diethylamine were added and the solution left overnight. A small amount of the product separated out but the total solid (1·4 g.) obtained on acidification was filtered off, washed with alcohol and ether; m.p. 240-80°.

The main crop on crystallisation from glacial acetic acid (charcoal) melted at 310°, not depressed by an admixture with 3-cyano-4-methyl-6-phenyl-2-pyridone (XII, X=CN). The mother-crop even on several crystallisation from acetic acid did not show any sharp melting point. It was then hydrolysed with sulphuric acid (80%) in the usual way when the known 4-methyl-6-phenyl-2-pyridone, m.p. 180-181°, was isolated in good yield. The cause of the indifferent melted point may be due to the presence of a trace of the isomeric compound 3-cyano-4-phenyl-6-methyl-2-pyridone.

The author wishes to express his appreciation to Prof. H. K. Sen for his kind interest taken, and also to Mr. C. Barat of this laboratory for kindly supplying him with some of the starting materials required in this investigation.

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Chemical Examination of *Sida Cordifolia*, Linn.

By Sudhamoy Ghosh and Ashutosh Dutt.

Sida cordifolia is said to be one of the most valuable drugs in the Ayurvedic system of medicine and has therefore been much used by the Hindu physicians from very early times. It is also used by Mahomedan physicians (Hakims) who consider it to possess aphrodisiac properties.

The air-dried material was secured locally and it was kindly identified by Prof. E. N. Ghosh, M.D., as *Sida cordifolia*, Linn. (Berelá). The whole plant (including leaves, seeds, stems and roots) was used in the present investigation. *S. cordifolia* is said to contain asparagin (Dymock, "Pharmacographia Indica," 1890, Vol. I, p. 207). No other work seems to be on record regarding either a detailed or systematic study of the nature of the chemical constituents present in the plant.

The most interesting finding in our present investigation is the presence of ephedrine in this plant which is widely different in nature from that in which it has been discovered before (*viz.*, *Ephedra vulgaris*), the former belonging to *Angiosperms* and the latter to *Gymnosperms*, two entirely different divisions of the vegetable kingdom.

Experimental.

A *preliminary examination* to test for alkaloids was made by extracting a few grams of the powdered drug with Prollius mixture and alkaloid was found to be present.

Several *assays* were made of the entire plant and the average of 5 analyses by the U. S. P. method (recommended for belladonna assay) showed the presence of 0·085 % of total alkaloids. The highest yield was obtained from samples of plants in flower. The seeds, leaves, stems and roots were also tested separately and it was observed that the seeds contain nearly 4 times more alkaloid than any of the other parts mentioned. The amount of seed varied in different samples and were not sufficient to allow us to use them for the preparation of the alkaloid on a large scale.

For a *systematic examination* of the drug, 200 g. of the coarsely powdered plant were extracted successively with petroleum ether (b. p. 35–50°), ether, absolute alcohol and water. The organic solvent was removed in each case and the residue weighed. Petroleum ether extracted 1·21 %, ether, 0·72 % and absolute alcohol 4·08 % of the weight of the air-dried entire plant. The *petroleum ether extract* was found to contain a small amount of fatty oil and substance similar to phytosterol. They were not examined in detail as having no pharmacological importance. The *ethereal extract* gave no test for alkaloids but it contained a very small amount of an organic acid, probably a resin acid.

The *alcoholic extract* was first freed from alcohol under diminished pressure. The residue was extracted repeatedly with cold, dilute, hydrochloric acid until it was free from alkaloid. The residue consisted mainly of chlorophyll and resinous matter. The aqueous acid-extract was washed thrice with petroleum ether, made alkaline with dilute ammonia and shaken repeatedly with chloroform until all the alkaloid was extracted. The chloroform extract was washed with water, dried over anhydrous sodium sulphate and the solvent removed. The total alkaloids were thus obtained as a brown amorphous mass. Its isolation on a larger scale and further purification is described later on. After removal of the alkaloid the aqueous portion was neutralised, filtered and treated with neutral lead acetate. The filtrate from lead acetate was next treated with a solution of basic lead acetate. The filtrate from basic lead acetate treatment was freed from lead by sulphuretted hydrogen, the excess of sulphuretted hydrogen was removed by carbon dioxide, the solution neutralised and evaporated under diminished pressure. None of the lead precipitates or the final filtrate yielded any crystalline substance and tannins and glucosides were found to be absent.

After exhaustion with absolute alcohol, the drug was extracted several times with cold water. The aqueous extract showed the presence of mucilaginous matter and some potassium nitrate. No glucoside could be obtained.

Isolation and Purification of the Alkaloid.—About 100 kilograms of the air-dried drug were coarsely powdered and extracted repeatedly with rectified spirit until the alkaloid was exhausted. The alcohol was recovered under reduced pressure. The residual extract weighed about 7·76 kilograms. This was repeatedly taken up with

1% hydrochloric acid till the acid extract gave no reaction with alkaloidal reagents. The acid extract was filtered through cotton wool and then shaken with petroleum ether to remove some oily matter. The solution was then made alkaline with ammonia and extracted repeatedly with chloroform. The chloroform extract was washed with water containing a little ammonia, dried over anhydrous sodium sulphate and the chloroform removed. The crude alkaloid thus obtained was dissolved in absolute alcohol and treated with dilute hydrochloric acid until faintly acid. The alcohol was evaporated off and the residue dissolved in hot water. The solution was filtered, cooled and shaken with ether until the ether ceased to extract anything. It was then made alkaline with dilute caustic soda and the liberated alkaloid was extracted repeatedly with ether. The ethereal extracts were washed with water containing a little ammonia, dried over anhydrous sodium sulphate and the ether removed. The residue from ether was dissolved in a small quantity of absolute alcohol and neutralised with alcoholic hydrochloric acid. The alcohol was evaporated off and the residue dried in *vacuo* over sulphuric acid. The dry residue was then treated successively with benzene, petroleum ether, ether and chloroform in order to remove some impurities. Only the chloroform was found to dissolve traces of the alkaloid. The residue was next dissolved in hot absolute alcohol and allowed to crystallise. The crystals which separated out gradually were washed with cold absolute alcohol and recrystallised from dilute alcohol when colourless crystals were obtained. These were then recrystallised from distilled water and dried. The *hydrochloride* was further purified by solution in absolute alcohol and precipitation with ether.

The original aqueous alkaline solution (which was extracted exhaustively with ether) was next repeatedly shaken with chloroform which dissolved out all the residual alkaloids constituting about one-third of the total alkaloids. It has not as yet been possible to crystallise the chloroform-suluble bases. From the pharmacological properties studied they appear, however, to be alkaloids of a similar nature.

The hydrochloride of the alkaloid was freely soluble in water and sparingly in absolute alcohol. It crystallised both from alcohol and water in colourless needles and melted at 215·5°. A mixed melting point determination with pure ephedrine hydrochloride prepared from *Ephedra Vulgaris* showed no depression in m.p. The specific rotation

in aqueous solution $[\alpha]_D^{22^\circ}$ was $-35{\cdot}0^\circ$ (m.p. ephedrine hydrochloride is $215^\circ - 216^\circ$ and $[\alpha]_D$ $-32{\cdot}5^\circ$ to $-36{\cdot}5^\circ$). The *aurichloride* crystallised from water in lemon-yellow needles. The *chloroplatinate* crystallised in well-defined orange needles, m.p. 190·5°. Some of the latter was dried to a constant weight in a vacuum desiccator and the platinum estimated. The molecular weight thus obtained with the very small amount of material available was 165 (M.W. of ephedrine, 167).

The following microchemical reactions were also observed:

	Reagents.		Reactions.
1.	Mercuric chloride	...	White amorphous precipitate.
2.	Millon's reagent	...	White amorphous precipitate, soluble in excess.
3.	Phosphotungstic acid	...	White amorphous precipitate.
4.	Phosphomolybdic acid	...	Lemon-yellow precipitate.
5.	Wagner's reagent	...	Amorphous precipitate.
6.	Mayer's reagent	...	White precipitate, soluble in excess.
7.	Chromic acid	...	Orange precipitate.
8.	Picric acid	...	Pale yellow precipitate.
9.	Kraut's reagent	...	Orange precipitate, which changed into needles on standing.
10.	Oxalic acid	...	Colourless needles.
11.	Potassium permanganate	...	Amorphous buff-coloured precipitate.

Colour Reactions.—

(1) Concentrated sulphuric acid produced a very pale straw yellow colour.

(2) Biuret reaction: To one c.c. of a 5% solution of the hydrochloride, 1 c.c. of 1% copper sulphate and 1 c.c. of 20% caustic soda were added. An intense violet colour was produced. It was then shaken with 10 c.c. of ether. The ethereal extract which dissolved the colour was evaporated on a watch glass. A gelatinous violet residue was left. This colour reaction is very characteristic of ephedrine and affords strong confirmation of the isolated alkaloid being ephedrine.

Concentrated hydrochloric or nitric acid, or ferric chloride did not show any marked change.

All the above properties and tests prove conclusively that ephedrine is one of the chief constituents of the alkaloids present in Berelá.

Pharmacological Action.—The pharmacological action of the alkaloid hydrochloride was seen on animals and it was found to cause a marked and persistent rise of blood-pressure in anaesthetised or decerebrated animals, but it had no effect on animals whose vasomotor nerve-endings were paralysed by repeated injections of small doses of ergotoxine. The force and frequency of the beat of the heart were increased and the blood vessels were constricted when perfused with solutions of the alkaloid, but these effects were not seen when the animals were treated with ergotoxine. It also caused a well-marked dilatation of the bronchioles and inhibition of the movements of the intestine. These effects resemble those seen with the other sympathomimetic bases, such as adrenaline or ephedrine.

Summary.

1. *Sida cordifolia*, Linn, contains about 0·085% of alkaloids, the seeds being most rich in alkaloids.

2. It was also found to contain fatty oil, phytosterols, resins, resin acids, mucins, potassium nitrate, etc., but no tannin or glucoside.

3. The main portion of the alkaloid was identified to be ephedrine, an alkaloid so far observed only in the different varieties of *Ephedra*, the two plants belonging to entirely different divisions of the vegetable kingdom. The remaining alkaloids, very small in amount, appear to be related to ephedrine as judged by the pharmacological and other properties.

4. The pharmacological action confirms the identification by chemical methods.

In conclusion, we desire to express our thanks to Col. R. N. Chopra and Capt. P. De for the study of the pharmacological action of the alkaloid in detail, and also to Mahamahopadhyaya Kaviraj Gananath Sen, M.A., L.M.S., at whose kind suggestion we took up the drug for our study.

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Studies in Quinoline Compounds. Part II. Some Derivatives of 4-Phenyl-2-methylquinoline.

By Upendra Nath Brahmachari and Tarapada Bhattacharyya.

The enhanced toxicity of 4-phenyl-2-methylquinoline towards certain kinds of protozoa when compared with that of quinoline and quinaldine induced us to synthesise a few derivatives of this important compound. Up till now only very few compounds of this series have been synthesised. In the synthesis of these compounds we have taken the help of the reaction of Doebner and v. Miller modified by Beyer (*J. pr. Chem.*, 1886, *ii*, **33**, 393). In this way we have obtained

(*i*) 6-nitro-4-phenyl-2-methylquinoline,
(*ii*) 8-nitro-4-phenyl-2-methylquinoline, and a few derivatives of them.

By heating *p*-and *o*-nitroanilines respectively with benzoylacetone, little or no condensation takes place. Similarly on heating *p*-nitroaniline hydrochloride with a mixture of paraldehyde and acetophenone, already saturated with dry hydrochloric acid gas, very little or scarcely any, condensation takes place. But by certain modifications of the latter method to be described below we have ultimately succeeded in getting the above condensation products, and the increased basic properties of these substances enabled us in separating them from their parent substances.

These nitro-compounds are of a very pale yellowish green colour. They readily dissolve in dilute acids. Stannous chloride and hydrochloric acid easily reduce them to the corresponding amines which can be separated through their finely crystalline stannichlorides. They also react, rather easily, with *p*-dimethylaminobenzaldehyde to give the corresponding styryl compounds.

Experimental.

6-Nitro-4-phenyl-2-methylquinoline.

A mixture of acetophenone (50 c.c.) and paraldehyde (30 c.c.) is cooled in ice and saturated with dry hydrochloric acid gas. This

mixture is then allowed to stand for 48 hours. It is then again saturated in cold with dry hydrochloric acid gas and allowed to stand for 24 hours more. This is now slowly added to an intimate mixture of *p*-nitroaniline (58 g.) and concentrated hydrochloric acid (90 c.c.) and the whole heated for 5 to 6 hours on a water-bath with occasional shaking. It is then largely diluted with water and the supernatant liquid carefully filtered through a coarse filter paper. The clear filtrate is then cooled by adding ice. A strong aqueous solution of sodium hydroxide is then cautiously added to precipitate nearly the whole of the unreacted *p*-nitroaniline. It is then filtered and the filtrate supersaturated with alkali. The required nitrophenyl-2-methylquinoline thus precipitated, is separated by filtration, washed with water and dried on a porous plate. Under this condition it has a fine greenish colour. It can be further purified by recrystallisation from a mixture of acetone and ether.

The pure compound, m.p. 141°, possesses a yellowish-green colour. It gives precipitates with potassium dichromate, phosphomolybdic acid and picric acid, dissolves very easily in alcohol and acetone and moderately in ether and in boiling water. The solution of the compound in dilute mineral acids possesses an orange-yellow colour. (Found: N, 11·1. $C_{16}H_{12}O_2N_2$ requires N, 10·6 per cent.).

6-Amino-4-phenyl-2-methylquinoline.

The above nitro-compound can be conveniently reduced as follows: To a mixture of stannous chloride (30 g.) and concentrated hydrochloric acid (50 c.c.) the nitro-compound (6·5 g.) is gradually added under constant shaking. If the mixture gets very hot, it must be cooled under the tap. On cooling the fine crystalline stannichloride of the amine crystallises out. It is filtered, washed with concentrated hydrochloric acid and dissolved in about 200 c.c. of boiling water. The tin is precipitated as sulphide and removed by filtration. The filtrate when made alkaline with dilute sodium hydroxide precipitates the amine as fine needles. It is then recrystallised from ether; m. p. 188°. It can be diazotised and coupled with β-naphthol. The solution of the substance in acetone possesses a beautiful violet-blue flourescence. (Found: N, 12·3. $C_{16}H_{14}N_2$ requires N, 12·0 per cent.).

6-Nitro-4-phenyl-2-p-dimethylaminostyrylquinoline.

This compound can be easily prepared by heating to gentle boiling over a small flame, a mixture of 6-nitro-4-phenyl-2-methylquinoline and *p*-dimethylaminobenzaldehyde in equimolecular proportions for about 10 to 15 minutes. The product is then poured into water. The solid thus separated is then purified by recrystallisation from acetone. It has a brownish-red colour and melts at 64°. (Found: N, 10·8. $C_{25}H_{21}O_2N_3$ requires N, 10·6 per cent.).

8-Nitro-4-phenyl-2-methylquinoline.

A mixture of acetophenone (50 g.) and paraldehyde (30 g.) is saturated with dry hydrochloric acid gas as described before. This is then added to a mixture of *o*-nitroaniline (58 g.) and concentrated hydrochloric acid (90 g.) and the whole heated on a water-bath for 7 to 8 hours. The product is then largely diluted (to about 2 litres) and, after filtration through a coarse filter paper, the filtrate is made strongly alkaline with sodium hydroxide. The *o*-nitroaniline remains in solution while the 8-nitro-4-phenyl-2-methylquinoline precipitates out as a greenish-black pasty mass. It is then dried on a porous plate and recrystallised from acetone. The compound looks pale yellowish-green; m. p. 94°. In its other behaviour it resembles the corresponding 6-nitro-compound. (Found: N, 10·9. $C_{16}H_{12}O_2N_2$ requires N, 10·6 per cent.).

8-Amino-4-phenyl-2-methylquinoline.

The above nitro-compound can also be reduced very easily by stannous chloride just as in the previous case. The filtrate, after the separation of tin sulphide, is evaporated on a water-bath when the amine hydrochloride remains behind. It is very difficult to get the free amine from this hydrochloride. The hydrochloride possesses an yellow colour and begins to decompose above 210°. It dissolves very easily in water to give an orange-yellow solution. (Found: N, 10·7. $C_{16}H_{15}N_2Cl$ requires N, 10·3 per cent.).

8-Nitro-4-phenyl-2-p-dimethylaminostyrylquinoline.

The preparation and purification of this compound is exactly similar to those of the corresponding 6-nitro-compound, 8-nitro-4-phenyl-2-methylquinoline being substituted for the 6-nitro-4-phenyl-2-methylquinoline. It melts at 129°. (Found: N, 10·9. $C_{25}H_{21}O_2N_3$ requires N, 10·6 per cent.).

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On a series of new Tetrammine-cobaltic Complexes.

By Pulin Bihari Sarkar and Tuhinangsu Das-Gupta.

The cobaltiammine thiosulphates and thiosulphato-cobalti-ammines have been very little studied (Jörgensen, *J. pr. Chem.*, 1878, *ii*, **18**, 212; and Rây, *J. Indian Chem. Soc.*, 1927, **4**, 64).

In course of our work on the following ionic isomers

$$\left[\begin{matrix}\mathrm{Cl}\\ \mathrm{Co(NH_3)_5}\end{matrix}\right]\mathrm{S_2O_3}, \quad \left[\begin{matrix}\mathrm{S_2O_3}\\ \mathrm{Co\,(NH_3)_5}\end{matrix}\right]\mathrm{Cl}, \quad \left[\begin{matrix}\mathrm{Br}\\ \mathrm{Co(NH_3)_5}\end{matrix}\right]\mathrm{S_2O_3}.$$

(I) (II) (III)

$$\left[\begin{matrix}\mathrm{S_2O_3}\\ \mathrm{Co\,(NH_3)_5}\end{matrix}\right]\mathrm{Br},$$

(IV)

we observed that the thiosulphato-pentammine compounds possess a characteristic ultraviolet absorption spectrum, having two heads and can thus be easily distinguished from their ionic isomers, which do not exhibit any such selective absorption.

It was observed that the molecular conductivity of complex (II) was half of that of complex (I). The electro-affinity of Cl, being greater than that of S_2O_3, complex (II) was expected to be more stable than its ionic isomer. On keeping complex (I) between 35-40° for 4 weeks, the colour was completely changed to that of complex (II), without any appreciable change in the weight. This transformation, easily recognized by chemical test, was corroborated by (*i*) determining the absorption spectrum which was found to be identical with that of the thiosulphato-complex; and by (*ii*) measuring the conductivity, which was halved. Similar transformation was also observed in the case of the bromo-salt. This led us to study the preparation of tetrammine cobaltic compounds with the thiosulphate group inside the positive complex. Rây (*loc. cit.*) obtained only the thiosulphato-pentammine series by the direct ammoniation of cobalt salts in presence of ammonium or sodium thiosulphate. We supposed in the light of the above work that better results would

follow by replacing the strongly electronegative Cl by the weakly electronegative S_2O_3. Our starting material was

either $\left[\begin{matrix}(1)\ Cl \\ (6)\ Cl\end{matrix}\ Co(NH_3)_4\right]Cl$ or $\left[\begin{matrix}(1)\ Cl \\ (2)\ H_2O\end{matrix}\ Co\ (NH_3)_4\right]Cl_2$.

Preliminary experiments showed the reaction to be a complicated one. We accordingly tried the double decomposition with $Na_2S_2O_3$ at low temperatures (*i.e.*, below 0°). With either of the above materials as the starting substance, the identical highly soluble green crystalline compound was obtained in each case, which was found to be trans-thiosulphato-aquo-tetrammine-cobaltic-thiosulphate

$$\left[\begin{matrix}(1)\ S_2O_3 \\ (6)\ H_2O\end{matrix}\ Co(NH_3)_4\right]_2 S_2O_3,$$

S_2O_3-group taking up one co-ordination position only. From the above product by double decomposition we have been able to prepare a series of green compounds of the formula

$$\left[\begin{matrix}S_2O_3 \\ Co\ H_2O \\ (NH_3)_4\end{matrix}\right]X, \qquad \text{where } X = Cl,\ Br,\ NO_3,\ SCN,\ \tfrac{1}{2}CrO_4,\ \tfrac{1}{2}SO_4 \text{ or } \tfrac{1}{2}S_2O_6.$$

Their ultraviolet absorption spectra in aqueous solutions are identical, having two characteristic heads.

After the isolation of the above product, the solution was taken out of the freezing mixture and kept at the laboratory temperature (30-35°). Shining green insoluble plates begin to appear which were found to be $\left[\begin{matrix}(1)\ S_2O_3 \\ (6)\ OH\end{matrix}\ Co(NH_3)_4\right]$. After the removal of the second product, the hydrolysis was prolonged for a little longer and from the solution by means of alcohol, we isolated a third red product of the composition, $Co_3(S_2O_3)_2(OH)_4(NH_3)_8$, $2H_2O$. Its constitution was determined in the following way—

(1) Dilute alkali in the cold precipitated cobaltous hydroxide and $Co(OH)_3$ from the filtrate on boiling.

(2) Cobaltic cobalt was found to be two-thirds the amount of total cobalt.

(3) After the removal of S_2O_3-group by digestion with $AgNO_3$ and subsequent removal of excess of Ag by HCl, the solution did not evolve chlorine on heating.

(4) Removing S_2O_3-group by $AgNO_3$ and adding $AmNO_3$ and H_2O_2, we have been able to isolate dodecammine-hexol-tetracobaltinitrate

$$\left[\begin{matrix} \text{III} \\ \text{Co} \end{matrix} \left\{ \begin{matrix} \text{OH} \\ \text{OH} \end{matrix} \begin{matrix} \text{III} \\ \text{Co}(NH_3)_4 \end{matrix} \right\}_3 \right] (NO_3)_6.$$

All these prove the constitution of the red compound to be

$$\left[\begin{matrix} \text{II} \\ \text{Co} \end{matrix} \left\{ \begin{matrix} (H_2O)_2 \\ \text{OH} \\ \text{OH} \end{matrix} \begin{matrix} \text{III} \\ \text{Co} \ (NH_3)_4 \end{matrix} \right\}_2 \right] (S_2O_3)_2.$$

Mechanism of these reactions.—The dichloro or chloroaquotetrammine cobaltic salts are, in aqueous solution, the seats of the following equilibria—

$$\left[\text{Co} \begin{matrix} \text{Cl}_2 \\ (NH_3)_4 \end{matrix} \right] \text{Cl} \rightleftarrows \left[\text{Co} \begin{matrix} \text{Cl} \\ H_2O \\ (NH_3)_4 \end{matrix} \right] \text{Cl}_2 \rightleftarrows \left[\text{Co} \begin{matrix} \text{Cl} \\ \text{OH} \\ (NH_3)_4 \end{matrix} \right] \text{Cl}.$$

At low temperatures the first reaction is the replacement of Cl by weak electronegative S_2O_3; with rise of temperature hydrolysis gave rise to the hydroxo-salt, and lastly the prolongation of hydrolysis led to the acid, H_2SO_3, which partially reduced the cobaltic compounds to give rise to the cobalto-cobaltic complex.

It is interesting to note that these types of cobaltic complexes were obtained by Werner and Jörgensen by the oxidation of cobalt salts in presence of ethylenediamine by means of air.

The reaction being very vigorous, Werner and his pupils could not isolate the intermediate cobalto-cobaltic complex with NH_3 in place of ethylenediamine, but only the stable final product,

$$\left[\begin{matrix} \text{III} \\ \text{Co} \end{matrix} \left\{ \begin{matrix} \text{OH} \\ \text{OH} \end{matrix} \begin{matrix} \text{III} \\ \text{Co}(NH_3)_4 \end{matrix} \right\}_3 \right] X_6.$$

Analytical and other details will form the subject of our next communication.

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On Munjisthin. Part II.*

By Prafulla Chandra Mitter and Harogopal Biswas.

On oxidation with an alkaline solution of potassium permanganate, 2-*p*-toluoylbenzoic acid (Friedel and Crafts, *Ann. Chim. Phys.*, 1888, *vi*, **14**, 446) gives benzophenone-2:4′-dicarboxylic acid (Limpricht, *Ber.*, 1895, **28**, 1134) which on treatment with sulphuric acid gives anthraquinone-β-carboxylic acid; it appeared to us to be of interest to enquire, whether a similar reaction could not be applied for the synthesis of 2:4-dihydroxy-3-carboxyanthraquinone, which represents, most probably, the constitution of munjisthin.

We condensed 2:4-dimethoxytoluene with phthalic anhydride in presence of aluminium chloride and obtained in this manner 2-(2′:4′-dimethoxy-3′-methyl)-benzoylbenzoic acid. The substance, however, resisted all attempts at oxidation.

Subsequently, the benzoylbenzoic acid was converted into the corresponding anthraquinone, by treatment with sulphuric acid and from this, by de-methylation, rubiadin was obtained. Attempts at direct oxidation of rubiadin have also, so far, failed.

Experimental.

2-Methoxy-6-nitrotoluene.—Starting from 2:6-dinitrotoluene, we prepared 2-amino-6-nitrotoluene (Cunerth, *Annalen*, 1874, **172**, 221; Ullmann, *Ber.*, 1884, **17**, 1958) and from this by diazotisation, 2-oxy-6-nitrotoluene (Ullmann, *loc. cit.*) which, on methylation, gave 2-methoxy-6-nitrotoluene, identical with one of the products obtained by Simonsen and Nayak (*J. Chem. Soc.*, 1915, **107**, 828) by the nitration of 3-acetylamino-2-methoxytoluene followed by deacetyation and removal of amino-group.

2-Methoxy-6-aminotoluene Hydrochloride.—2-Methoxy-6-nitrotoluene is reduced with tin and hydrochloric acid, the tin separated by means of sulphuretted hydrogen and the filtrate evaporated to

* Read before the Indian Science Congress, Allahabad, January, 1930.

dryness. It forms needles from alcohol, m.p. 234-35°. (Found: N, 8·28. Calc. N, 8·07 per cent.).

2-Methoxy-6-hydroxytoluene.—The amine hydrochloride (2·5 g.) is added to boiling dilute sulphuric acid (17 g. conc. acid in 175 c.c. water), kept for a few minutes at this temperature and rapidly cooled with stirring. When the temperature reaches 5°, 2*N*-sodium nitrite solution (9 c.c.) is gradually added and the mixture stirred for two hours. Further 17g. of sulphuric acid (in 175 c.c. of water) are now added and the mixture warmed on the water-bath at 40-45° for about two hours. The mixture is then cooled, extracted with ether, the ethereal solution dried by means of anhydrous sodium sulphate, and the ether distilled off. The residue has b.p. 242-44°. (Found: C, 69·72; H, 7·30. $C_8H_{10}O_2$ requires C, 69·56; H, 7·25 per cent.).

2:6-Dimethoxytoluene.—The hydroxymethoxytoluene is methylated in the usual manner. The dimethoxy compound distilled at 220-22°. The distillate solidified in the receiver and crystallised as colourless plates from alcohol, m.p. 35°. (Found: C, 70·84; H, 7·71. $C_9H_{12}O_2$ requires C, 71·05; H, 7·89 per cent.).

2-(2′:4′-Dimethoxy-3′-methyl)-benzoylbenzoic Acid.—2:6-Dimethoxytoluene (5·5 g.) and phthalic anhydride (5 g.) are covered with carbon bisulphide (100 c.c.) Finely powdered aluminium chloride (10 g.) is gradually added and the flask heated on the water-bath under reflux for about 10 hours. Carbon bisulphide is then decanted off, ice and hydrochloric acid are added and steam passed through the mixture. The residue is filtered, washed, extracted with sodium carbonate solution and filtered. The filtrate, on acidification, gave a white precipitate which crystallised as plates from glacial acetic acid, m.p. 180°. (Found: C, 67·81; H, 5·05. $C_{17}H_{16}O_5$ requires C, 68·00; H, 5·33 per cent.).

*Rubiadin Methyl Ether.**—The benzoylbenzoic acid (5 g.) was mixed with sulphuric acid (10 g. *d* 1·84) and fuming sulphuric acid (50 g., 20 per cent. SO_3) and heated on the water-bath for four hours. It was then poured on ice, filtered and the residue extracted successively with boiling water, boiling dilute sodium carbonate solution and cold 2 per cent. caustic soda solution. The residue is washed with water and dried. It crystallised as needles from glacial acetic acid, m.p. 188-189°. (Found: C, 72·06; H, 4·74. $C_{16}H_{12}O_4$ requires C, 71·64; H, 4·5 per cent.).

* The substance appears to be identical with the 3-*O*-methylrubiadin, m.p. 186°, of Jones and Robertson (*J. Chem. Soc.*, 1930, p. 1704).—*Editor.*

Rubiadin.—Methoxyrubiadin (5 g.) was thoroughly mixed with powdered aluminium chloride (3 g.). The temperature of the mixture was slowly raised to 200° in course of an hour and the mixture kept at this temperature for another hour. The mass is then poured into ice-water, boiled and filtered. The residue is treated with dilute caustic soda solution, filtered, and the filtrate acidified, boiled and filtered. The residue was crystallised from a large volume of glacial acetic acid; m.p. 290-291°. (Found: C, 70·69; H, 4·01. $C_{15}H_{10}O_4$ requires C, 70·87; H, 3·93 per cent.).

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Some Sulphur Derivatives of 2-Methoxytoluene.

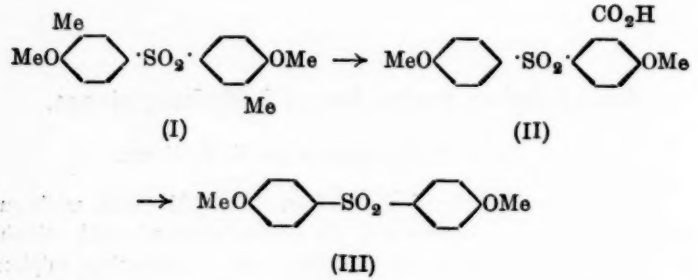
By G. B. Kolhatkar and K. V. Bokil.

Meldrum and Shah (*J. Chem. Soc.*, 1923, **123**, 1992), while sulphonating 2-methoxytoluene with 3% fuming sulphuric acid, obtained an alkali-insoluble by-product (m.p. 138°) containing sulphur; they did not, however, investigate its nature. Zehenter (*Monatsh.*, 1912, **33**, 335) also obtained a by-product of a similar type during the sulphonation of 2-hydroxytoluene with 8% fuming sulphuric acid ; he, however, recognised the product as a sulphone but did not investigate its precise constitution. The by-product from 2-methoxytoluene must evidently be a sulphone and the authors' first objective was to determine the constitution of both the above products.

The sulphonation method gives a very poor yield of the sulphone. The large quantity of the product, required for the purpose of determining its constitution, could, however, be obtained by the general synthetical method of Beckurts and Otto (*Ber.*, 1878, **11**, 472). The product, obtained by the action of 2-methoxytoluene-5-sulphonylchloride on 2-methoxytoluene, was found to be identical with that obtained by the sulphonation method. This synthesis, however, does not throw much light on the position of the SO_2-group with respect to the constituents in the other benzene residue in the sulphone.

The method of decomposing the sulphone with phosphorus pentachloride (Meyer and Jacobson, " Lehrbuch der Organischen Chemie, 1921, Vol. II, Part I, p. 144) and the method of decomposing the sulphone with sodium in a suitable solvent (Krafft and Worster, *Ber.*, 1893, **26**, 1813) failed in eliciting the constitution of the sulphone. It was, however, thought that by oxidising the above sulphone to the corresponding dibasic acid and removing the two carboxyl groups, the resulting sulphone could possibly be identified with a known compound. This proved to be the case, and the sulphone (III) obtained by these reactions was identified as *p*-anisolsulphone, m.p. 129° (Mauthner, *Ber.*, 1906, **39**, 3593; also Smiles and Le-Rossignol, *J.*

Chem. Soc., 1908, **93**, 756). The constitution of the original sulphone must therefore be represented as (I).



(I) (II)

(III)

By demethylating the sulphone (I), 4 : 4′-dihydroxy-3 : 3′-dimethyldiphenylsulphone (m.p. 263°) was obtained. This, therefore, must be the constitution of Zehenter's sulphone which is stated to melt at 263-65°.

The synthesis of the following new sulphones from 2-methoxytoluene and various sulphonylchlorides are found to verify the general rules of substitution, that the sulphonyl group takes up the *para*-position (or *ortho*, depending upon the original substituents present) to a methoxy or ethoxy group. But an exception to this rule is found in the cases of anisol and phenetol :

(*a*) Benzenesulphonylchloride and 2-methoxytoluene gave a sulphone identical with that obtained from benzene and 2-methoxytoluene -5-sulphonylchloride. Hence the product is 3-methyl-4-methoxydiphenylsulphone.

(*b*) *p*-Toluenesulphonylchloride and 2-methoxytoluene gave a sulphone identical with that obtained, as the sole product, from toluene and 2-methoxytoluene-5-sulphonylchloride. Hence the product is 3 : 4-dimethyl-4-methoxydiphenylsulphone.

(*c*) *p*-Anisolsulphonylchloride and 2-methoxytoluene gave a sulphone (m.p. 126°) identical with that obtained from anisol and 2-methoxytoluene-5-sulphonylchloride. Hence this product must be 3-methyl-4 : 4′-dimethoxydiphenylsulphone. But in the second method, along with the usual product (*para*), an isomeric compound (m.p. 102°) was isolated in an appreciable quantity. This was found to be different from the *ortho*-modification which, when synthesised from *o*-anisolsulphonylchloride and 2-methoxytoluene, melted at 145°.

(*d*) The reactions between (i) 2-methoxytoluene-5-sulphonylchloride and phenetol, and (ii) *p*-anisolsulphoylchloride and anisol were

also found to produce two isomeric compounds in each case. The nature of the second isomeric products is under investigation. The oxidation and demethylation products of many of the above compounds have also been described.

Some other Sulphur Derivatives of 2-Methoxytoluene.

The sulphoxide, sulphonium chloride, sulphide, sulphinic acid, disulphoxide, disulphide, disulphone and the thiol derivatives of 2-methoxytoluene are unknown, although the corresponding derivatives of *m*- and *p*-cresol methyl ether have been described (Smiles, *J. Chem. Soc.*, 1910, **97**, 2249; Smiles and Le-Rossignol, *loc.cit.*; Hilditch, *J. Chem. Soc.*, 1911, **99**, 1000). Accordingly we have prepared the above derivatives, an account of which will be found in the experimental.

EXPERIMENTAL.

2-Methoxytoluene-5- sulphonylchloride.—2-Methoxytoluene (62 g.) was gradually added to chlorosulphonic acid (325 g.) in a flask maintained at 0° during the addition. The mixture was kept at 0° for an hour and then poured over crushed ice when the solid sulphonylchloride immediately separated out. When allowed to stand overnight, along with the solid crust of the sulphonylchloride, some flocculent precipitate was also obtained. This was purified and identified as 3:3′-dimethyl-4:4′-dimethoxydiphenylsulphone, m. p. 138° (yield, 2·5%). The sulphonylchloride (yield, 80%) formed hexagonal plates from ether and yielded an amide, m.p. 137° (*cf.* Bromwell, *Amer. Chem. J.*, 1897, **19**, 573).

3:3′-Dimethyl-4:4′-dimethoxydiphenylsulphone (I).—2-Methoxytoluene-5-sulphonylchloride (11 g.) and 2-methoxytoluene (10 g. excess) in 30 c.c. of carbon disulphide were gradually treated with anhydrous aluminium chloride (7 g.) under reflux and then kept overnight. Next day the contents were heated on a water-bath for two hours, the carbon disulphide was removed and the residue decomposed successively by ice-cold water and concentrated hydrochloric acid (20 c. c.). The mixture was steam-distilled and the residue washed with ether (yield, 13·8 g.). It formed long needles from dilute acetic acid, m.p. 138°. (Found: C, 62·9; H 5·4; S, 10·64. M. W. (cryoscopic), 306·3. $C_{16}H_{18}O_4S$ requires C, 62·74; H, 5·88; S, 10·46 per cent. M.W., 306).

3:3'-*Dicarboxy*-4:4'-*dimethoxydiphenylsulphone* (II).—The finely powdered sulphone (I, 7·5 g.) was suspended in two litres of water containing potassium hydroxide (3 g.) and potassium permanganate (15·5 g.) in solution. The mixture was boiled until it was decolourised, separated from the precipitated manganese dioxide and the filtrate neutralised with concentrated hydrochloric acid. The precipitate (3·5 g.) separated from alcohol as small granular crystals which sintered at 245° and melted at 250° (decomp.).

The unoxidised material could be removed from the precipitated manganese dioxide by extracting with acetic acid. (Found: C, 52·11; H, 4·1; S, 8·55 ; equiv. 182·8. $C_{16}H_{14}O_8S$ requires C, 52·45; H, 3·82; S, 8·74 per cent., equiv., 183).

Decarboxylation of above: *Formation of* 4:4'-*Dimethoxydiphenylsulphone* (III).—The acid (3 g.), mixed with an equal quantity of quicklime, was distilled from a hard glass-bulbed tube. The distillate, a thick yellowish-red liquid, solidified when treated with a little ether (yield, 0·3 g.). It formed stout needles from alcohol, m. p. 129°. The mixed m. p. of this substance with that prepared by Smiles's method (*loc. cit.*) did not change. (Found: C, 60·14; H, 4·74; S, 11·57. $C_{14}H_{14}O_4S$ requires C, 60·43; H, 5·04; S, 11·51 per cent.).

3:3'-*Dimethyl*-4 : 4'-*dihydroxydiphenylsulphone*.—The sulphone (I, 1 g.) was heated with hydriodic acid (10 c. c. *d* 1·7) at 165° under reflux for two hours. The product was successively treated with concentrated alkali and dilute hydrochloric acid. It crystallised from dilute alcohol in small cubes, m. p. 263° (corr.); yield quantitative. (Found: C, 59·93; H, 4·67; S, 11·42. $C_{14}H_{14}O_4S$ requires C, 60·43; H, 5·04; S, 11·51 per cent.).

3: 3'-*Dicarboxy*-4:4'-*dihydroxydiphenylsulphone*.—The dibasic acid (II, 0·4 g.) was demethylated with hydriodic acid (5 c.c.) and the phenolic compound crystallised from water in short silky needles, m. p. 306-7° (decomp.). (Found: S, 10·0. $C_{14}H_{10}O_8S$ requires S, 9·47 per cent.).

3-*Methyl*-4-*methoxydiphenylsulphone* was prepared in two ways:

(*a*) Benzenesulphonylchloride and 2-methoxytoluene (in molecular proportions) gave an yield of 75%. (*b*) 2-Methoxytoluene-5-sulphonylchloride reacting with benzene gave 80% yield; m. p. 112-112·5°. (Found: C, 63·96 ; H, 5·55 ; S, 11·8. $C_{14}H_{14}O_3S$ requires C, 64·12; H, 5·32; S, 12·2 per cent.).

3-*Methyl*-4-*hydroxydiphenylsulphone* was obtained by demethylating the above sulphone with hydriodic acid at 170°. It formed microscopic needles from alcohol, m. p. 226°. (Found: S, 13·25. $C_{13}H_{12}O_3S$ requires S, 12·9 per cent.).

On oxidising the sulphone, m. p. 112°, with alkaline permanganate, 3-*carboxy*-4-*methoxydiphenylsulphone* was obtained (yield, 33%). It separated as long needles from hot water, m. p. 176°. (Found: S, 11·02; equiv., 292·82. $C_{14}H_{12}O_5S$ requires S, 10·95 per cent.; equiv., 292).

The above sulphone, on demethylation at 155-160°, formed 3-*carboxy*-4 *hydroxydiphenylsulphone*, which crystallised from hot water in stout needles, m. p. 216-17°. (Found: S, 11·62; equiv., 277·68. $C_{13}H_{10}O_5S$ requires S, 11·51 per cent. equiv., 278).

3: 4′-*Dimethyl*-4-*methoxydiphenylsulphone* was prepared in two ways: (*a*) From *p*-toluenesulphonychloride and 2-methoxytoluene (yield 90%) and (*b*) from 2-methoxytoluene-5-sulphonychloride and toluene (yield, 70%). The substance forms thin prismatic plates from alcohol, m. p. 109·5-110°. (Found: C, 64·99; H, 5·92; S, 11·3. $C_{15}H_{16}O_3S$ requires C, 65·21; H, 5·79; S, 11·59 per cent.).

3: 4′-*Dimethyl*-4-*hydroxydiphenylsulphone* was obtained from the above sulphone by demethylation at 175°. It formed short needles from alcohol, m. p. 200-201°. (Found: S, 12·5. Calc., S, 12·2 per cent.)

3: 4′-*Dicarboxy*-4-*methoxydiphenylsulphone*.—The sulphone (m.p. 110°) on oxidation with alkaline permanganate yielded the above compound which formed small granular crystals from alcohol, m. p. 283° (yield, 33°/₀). (Found: S, 9·48; equiv., 169·05. Calc., S, 9·52 per cent.; equiv., 168).

4:4′-*Dimethoxy*-3-*methyldiphenylsulphone* was prepared in two ways as before: (*a*) *p*-anisolsulphonylchloride and 2-methoxytoluene gave the sulphone, m. p. 126° (yield 80%). (*b*) Anisol and 2-methoxytoluene-5-sulphonylchloride gave a mixture of two compounds (total yield, 90%), one of which was identical with the preceding sulphone, m. p. 126°. The isomer, which formed about one third of the product, melted at 102°. (Found for substance, m. p. 126°: C, 61·15; H, 5·55; S, 11·17. Found for substance, m. p. 102°: C,61·24; H, 5·79; S, 11·26. $C_{15}H_{16}O_4S$ requires C, 61·64; H, 5·48; S, 10·96 per cent.).

3-*Carboxy*-4: 4′-*dimethoxydiphenylsulphone* was obtained by oxidising the sulphone (m. p. 126°, 4·5 g.) with alkaline permanganate (4·9 g.) (yield 30%), m. p. 186-7°. (Found: S, 9·61 ; equiv., 321·8. Calc., S, 9·96 per cent., equiv., 322).

3′-*Methyl*-2′: 4-*dimethoxydiphenylsulphone* was prepared by the action of *o*-anisolsulphonylchloride (m. p. 55°, prepared by Gattermann's reactions—*Ber.*, 1899, **32**, 1153) on 2-methoxytoluene. It formed thin plates or short needles from alcohol, m. p. 145°. (Found: C, 61·4; H, 5·55; S, 10·94. Calc., C, 61·64; H, 5·48; S, 10·96 per cent.).

3: 3′-*Dimethyl* 4 : 4′-*dimethoxydiphenylsulphoxide*.— Anhydrous aluminium chloride was gradually dissolved in 2-methoxytoluene (20 g. each), and the mixture, saturated with sulphur dioxide below 15°, was treated according to Smiles and Le-Rossignol's method. But of the three possible compounds as suggested by them, only two (sulphoxide and sulphonium chloride) were formed. The sulphoxide, extracted from the acid-liquid with ether, was crystallised from ethyl acetate in colourless rhombic plates, m. p. 87-87·5° (yield, 5·5 g.). On oxidation with alkaline permanganate, it gives the sulphone, m. p. 138° (I). (Found: C, 65·95; H, 6·27; S, 11·4. $C_{18}H_{18}O_3S$ requires C, 66·2 ; H, 6·2 ; S, 11·03 per cent.).

Tri-o-cresylsulphonium Chloride.—The original acid-liquid, after extraction with ether, was extracted with chloroform which on evaporation gave the sulphonium chloride as a semisolid mass ; it crystallised from water in colourless plates (yield, 8·5 g.). When recrystallised from acetone two isomeric compounds were obtained:— Fraction I (2 g.), m. p. 140-141°, was more suluble in cold water, but less soluble in cold or hot acetone than the other. (Found: S, 7·89. $C_{24}H_{27}O_3SCl$ requires S, 7·44 per cent.). Fraction II (6 g.) when recrystallised from moist acetone gave thick plates, m. p. 69-70°, containing three molecules of water of crystallisation. (Found: H_2O, 11·54. $C_{24}H_{27}O_3SCl$, $3H_2O$ requires H_2O, 11·09 per cent. (For anhydrous salt) S, 7·84. $C_{24}H_{27}O_3SCl$ requires S, 7·45 per cent.).

3: 3′-*Dimethyl*-4: 4′-*dimethoxydiphenylsulphide* was obtained by the reduction of the sulphoxide with zinc dust and glacial acetic acid. The ether extract left a thick liquid on evaporation which gradually solidified after a week; m. p. 37·5-38°. (Found: S, 11·89. Calc., S, 11·67 per cent.).

2-Methoxytoluene-5-sulphinic Acid.—2-Methoxytoluene-5-sulphonyl chloride (5 g.) was reduced by means of sodium sulphite (18 g. in 70 c. c. water) with occasional addition of a little caustic soda solution. The liquid was filtered from the insoluble solid (*A*, granular crystals from benzene, m. p. 206·5° decomp.) and acidified with dilute sulphuric acid when a turbid solution was obtained. This on keeping deposited an oil (3·85 g.). It could not be purified by distillation—even under reduced pressure—as it quickly decomposes on warming. Moreover it spontaneously changes into a white solid (*B*) insoluble in alkali, m. p. 118°. The *sodium* salt (thin leaflets from absolute alcohol) and *silver* salt (short needles from hot water) were prepared and analysed. (Found: Na, 10·8. $C_8H_9O_3SNa$ requires Na, 11·38 per cent. Ag, 36·24. $C_8H_9O_3SAg$ requires Ag, 36·64 per cent.).

3: 3′- *Dimethyl*-4 : 4′-*dimethoxydiphenyldisulphone*.— A mixture of the sodium salt of the above sulphinic acid (3 g.) and 2-methoxytoluene-5-sulphonylchloride (3 g.) in 20 c. c. absolute alcohol was boiled for 5 minutes and diluted with water. The flocculent precipitate was crystallised from benzene, m. p. 206·5° (decomp.). This is identical with the insoluble product (*A*) described in the preceding paragraph. (Found: C, 51·54; H, 5·05; S, 17·45. $C_{16}H_{18}O_6S_2$ requires C, 51·89; H, 4·86; S, 17·3 per cent.).

3: 3′-*Dimethyl*-4 : 4′-*dimethoxydiphenyldisulphoxide*.—The disulphide (*vide* below) (4 g.), in 30 c. c. glacial acetic acid was oxidised by a 30% solution of hydrogen peroxide (1½ mol.) and the mixture set aside for 24 hours when stout needles, m. p. 118°, were obtained (yield, 3 g.). Evidently the substance (*B*, see above) formed by the spontaneous decomposition of 2-methoxytoluene-5-sulphinic acid must be a disulphoxide since the mixed m. p. of these two compounds did not change. (Found: C, 56·68; H, 5·55; S, 18·9. $C_{16}H_{18}O_4S_2$ requires C, 56·1; H, 5·35; S, 18·93 per cent.).

2-Methoxy-5-thioltoluene was prepared by the reduction of the corresponding sulphonyl chloride with zinc dust and dilute hydrochloric acid in the usual way. The colourless oil, extracted by ether from the steam-distillate, was purified by distillation (b. p. 236-237°) which then immediately solidified; m. p. 42-43°. (Found: C, 61·88; H, 6·74; S, 21·19. $C_8H_{10}OS$ requires C, 62·34; H, 6·49; S, 20·78 per cent.).

3: 3′-*Dimethyl*-4 : 4′-*dimethoxydiphenyldisluphide*.—The above thiophenol (8·5 g.) was dissolved in 75 c. c. *N*-sodium hydroxide and

a solution of iodine (7·5 g.) in potassium iodide was gradually added with shaking. The disulphide separated as oily drops which gradually solidified (yield, 8 g.). It formed pale yellow thick crystals from alcohol, m. p. 44-45°. (Found: C, 62·59; H, 6·05; S, 21·3. $C_{16}H_{18}O_2S_2$ requires C, 62·74; H, 5·88; S, 20·93 per cent.).

One of us (K. V. B.) desires to express his gratitude to Mr. D. B. Limaye of the Ranade Industrial and Economic Institute, Poona, for many helpful suggestions.

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Reactivity of Conjugated Systems. Part II. Condensation of Acetylenic Ketones with Cyanoacetamide.

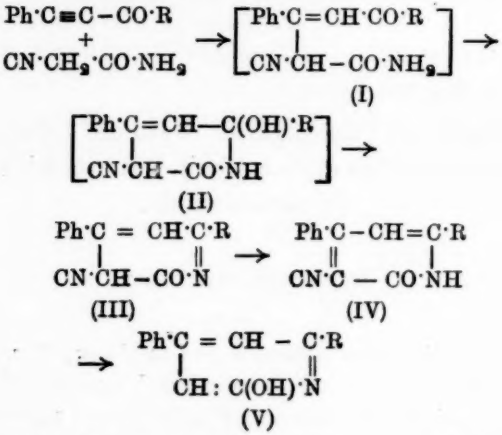
By Chittaranjan Barat.

In Part I of this series (Barat, *J. Indian Chem. Soc.*, 1930, **7**, 321), it was shown that in conjugated systems of the type $R{\cdot}CH{=}CH{\cdot}CR'{=}O$, the ethylenic linkage possesses a greater activity with regard to a reactive methylene group than the ketonic group. In the present work, the reaction between conjugated systems of the type $R{\cdot}C{\equiv}C{\cdot}CR'{=}O$ and cyanoacetamide has been studied mainly with the object of establishing the identities of certain 4:6-substituted pyridone derivatives obtained in the course of the previous work, both with Michael's and Knoevenagel's reagents.

By condensing benzoylphenylacetylene with malonic ester, Kohler obtained α-pyrone derivatives which he converted into the corresponding hydroxypyridine by the action of ammonia (*J. Amer. Chem. Soc.*, 1922, **44**, 379). Michael had observed before him (*J. pr. Chem.*, 1894, *ii*, **49**, 22) that malonic ester also condenses with esters of acetylenic acids, and quite recently, Bardhan (*J. Chem. Soc.*, 1929, p. 2223) has recorded the condensation of propionylphenylacetylene with cyanoacetamide. But he has not proceeded further than distinguishing this condensation product from the one obtained from propionylacetophenone and cyanoacetamide.

Moureau (*Bull. Soc. chim.*, 1905, *iii*, **33**, 131) and his collaborators have established beyond doubt that the triple-bond in these ketones is far more reactive than the ethylenic double bond in the corresponding arylidene ketones, and so it is quite justifiable to conclude that the primary addition of cyanoacetamide must take place at the triple-bond forming a compound of the type (I), which, by virtue of the great tendency of formation of a pyridine ring, immediately suffers ring-closure yielding a cyanopyridone of the type (III), which on

hydrolysis gives a hydroxypyridine (IV) identical with that obtained from the corresponding arylidene ketones (*loc. cit.*).



It is distinctive to note that neither the open-chain amide (I) nor the aldol compound (II) has been isolated under the experimental conditions even in the presence of Knoevenagel's reagent, whilst, with arylidene ketones the intermediate aldol type is readily isolable (*cf.* Barat, *loc. cit.*, also Kohler, *loc. cit.*). This has been no doubt due to the extreme tendency of the formation of a pyridine compound, which precludes the isolation of any intermediate aldol derivative. This phenomenon further supports the similarity of Michael's and Knoevenagel's reactions, first postulated by Sen (*J. Chem. Soc.*, 1915, **107**, 1347).

That the original condensation product belongs to type (IV) (at least in presence of alkali) has been proved by its readily yielding an *N*-methyl derivative, identical with the product derived from cyanoacetmethylamide and the corresponding ketones. The absence of a hydroxyl group is rendered extremely probable by its failure to give any colour reaction with alcoholic ferric chloride. Its solubility in alkalis, in the absence of a hydroxyl group, further indicates the presence of an imido-group. The hydrolysed product (V), however, does not yield a methyl derivative readily and exhibits a characteristic colouration with alcoholic ferric chloride, indicating the presence of a hydroxyl group and the absence of an imido-group, and in consequence the structure (V) has been ascribed to it.

It must, however, be admitted that there is a great likelihood of the addition product (I) being converted into (V) through the

intermediary of a compound of type (VI) formed by intramolecular rearrangement, on account of the greater stability of the type (VI) than type (I) in such three-carbon systems (*cf.* Lapworth and McRae, *J. Chem. Soc.*, 1922, **121**, 2747 ; Kon and his collaborators, *ibid*, 1923, **125**, 1361, and subsequent papers ; also Basu, *J. Indian Chem. Soc.*, 1930, **7**, 481).

$$\left[\begin{array}{l} Ph\cdot C - CH_2 - CO\cdot R \\ \quad\| \\ CN\cdot C - CO - NH_2 \end{array}\right]$$

(VI)

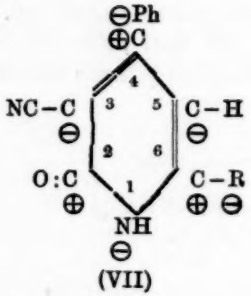
It is evident therefrom that the type (VI) can exist as long as the cyano-group is intact. On its hydrolysis, however, intramolecular rearrangement may be assumed to give rise to the hydroxy configuration (V).

Nevertheless it is equally true that the system (III$\rightleftharpoons$IV) is a tautomeric one, and as such it is difficult to ascribe any particular constitution to the substance. In the present work therefore, these compounds have been described as 4:6-disubstituted-3-cyano-2-pyridones in the general sense.

During the course of the present work, cyanoacetamide has been condensed with (1) benzoylphenylacetylene, (2) *p*-toluylphenylacetylene, (3) *p*-nitrobenzoylphenylacetylene, (4) acetylphenylacetylene, and (5) propionylphenylacetylene, with the additional object of examining the stability of the condensation products in relation to the substituent groups. It has been observed that whether with Michael's or Knoevenagel's reagents, identical products are obtained under both conditions.

It has been of great interest to observe that while the reaction proceeded with remarkable ease in the former cases giving excellent yields of the products, the yields were extremely low with the two latter ketones. (Quite an analogous phenomenon was also noticed in the case of cyanoacetamide condensations with arylidene ketones, *loc. cit.*). Evidently therefore the stability of the condensation products increases with increasing negative character of R in (IV). This fact could be explained by an extension of Fry's substitution rule for benzene derivatives (Fry, " The Electronic Conception of Valence and the Constitution of Benzene," 1921) to the pyridine rings considered herein,—an idea which does not appear to have been applied to pyridine derivatives before (*cf.* Fry, *J. Amer.*

Chem. Soc., 1912, **34**, 664, *et seq*; also *Z. physikal. Chem.*, 1911, **76**, 885, *et seq*).



(VII)

In the pyridine skeleton (VII) since the NH-group is acidic in nature, giving rise to stable alkali salts, the nitrogen atom in position (1) must be negative to start with. Taking this to be the " key atom " (*cf.* Lapworth, *J. Chem. Soc.*, 1901, **79**, 1265; *Proc.*, 1901, **17**, 93; *Mem. Manchester Phil. Soc.*, 1920, *ii*, **64**, 1; *J. Chem. Soc.*, 1922, **121**, 416 ; also Burckhardt and Lapworth, *ibid*, 1925, **127**, 1742) and starting along the order indicated in (VII) it will be found that the C atoms (4) and (6) are of a *positive* nature, and hence can form stabler combinations with *negative* substituents. Further, when the carbon atom (4) is already attached to a phenyl (negative) group, it will favour a similar combination (with a negative group) with the carbon atom (6) (*i.e.*, *meta* to it). This also is quite in a line with Fry's substitution rule for benzene derivatives, *viz.*, " when the substituents are of the same sign or polarity, they will occupy positions which are *meta* to each other..... " (Stewart, " Recent Advances in Organic Chemistry ", 1927, Vol. I, p. 343).

On these considerations it would be quite reasonable to expect that the condensation product (IV) would be more stably constituted when R is a phenyl, tolyl or *p*-nitrophenyl group than when it is a methyl or ethyl group, and this expectation has been borne out by facts.

It is further of interest to observe that the hydrolysis of the cyano-group in (IV) takes place with very nearly quantitative yields when R is phenyl, tolyl or *p*-nitrophenyl, while the yield is comparatively poor when R is methyl or ethyl. This further proves the greater stability of the 6-aryl derivatives.

These compounds have been found to be identical with the dehydrogenation products of the tetrahydropyridone derivatives

obtained by condensing cyanoacetamide with the corresponding arylidene ketones (*loc. cit.*).

Another point worthy of note has been the identity of the cyanopyridone obtained from acetylphenylacetylene, with the Knoevenagel condensation product between cyanoacetamide and benzalacetone obtained by Sen (*loc. cit.*). Sen's compound, as observed by him, contained two atoms of hydrogen less than required by theory, and was therefore the dehydrogenated product, formed no doubt by the prolonged action of diethylamine on the original condensation product by a process of reciprocal oxidation and reduction,—a phenomenon which these bodies exhibit in presence of alcoholic ammonia (*cf.* Barat, *loc. cit.*, also Kohler and Souther, *J. Amer. Chem. Soc.*, 1922, **44**, 2903.).

The present work, together with the former of the series, thus clearly points to the reactivity of the unsaturated centres in conjugated systems, to which theory additional experimental evidence will be brought forward in subsequent communications.

Experimental.

Considerable difficulty had to be experienced in the preparation of these ketones, on account of the tedious methods as well as the comparatively low yields. The acylphenylacetylenes were prepared by the general method of Nef (*Annalen*, 1899, **308**, 264), while phenylacetylene was prepared according to the method of Hessler ("Organic Synthesis", Vol. II, p. 67).

General Methods.—The condensations were carried out, both by Michael's as well as Knoevenagel's method in an exactly similar manner to those employed in the case of arylidene ketones (Barat, *loc. cit.*, p. 328) with the only exception that in the case of Michael's reaction the temperature was kept low, as otherwise tar formation, owing to secondary reactions, ensued. On mixing the ketone with the pasty sodiocyanoacetamide, the colour became intense red, and the solid went gradually into solution ; the colour, however, became lighter as the reaction proceeded, resulting in the separation of the sodium derivative of the condensation product. This was collected usually after one day. The sodium salt was washed with cold alcohol, taken up with water, and decomposed by dilute mineral acids. It could then be separated, washed with water, dried and purified by crystallisation. The mother-liquor, on

dilution and acidulation, gave a further quantity of the substance, hardly profitable to recover on account of the small quantity obtained, as well as the impurities that are difficult to remove. The Knoevenagel's reaction was usually finished in three or four days, but the mixture was handled after a week; the solid that separated out by itself was usually taken, the mother-liquor generally yielding very impure products which contained appreciable quantities of the corresponding β-diketone, formed by the action of water on the acetylenic ketone. These cyanopyridones were identical with those obtained from the corresponding arylidene ketones, and yielded *N*-methyl derivatives when left over at ordinary temperature with an equivalent of sodium methoxide and an excess of methyl iodide in methyl alcoholic solution, till the mixture became neutral. The conversion was usually finished in a day or two and the product was isolated by evaporating the mixture on the water-bath, washing the residue with water till free from iodides, followed by crystallisation of the solid that remained behind. The same product was also obtained when the sodium salt obtained from the Michael's reaction was similarily treated with methyl iodide. An identical compound was also obtained when the corresponding ketone was condensed with cyanoacetmethylamide by Michael's method ; the product so obtained was no longer soluble in alkalis, and hence could be separated merely by dilution of the reaction mixture and extracting with chloroform or ether. The reaction, however, was slower in this case and the mixture did not deposit any sodium derivative. The solution was then evaporated to dryness and the residue crystallised.

The cyanopyridones could be hydrolysed by heating with 75-80% sulphuric acid in the usual way. These bodies were identified with specimens from stock and were also identical with specimens prepared by other ways (*cf.* Basu, *J. Indian Chem. Soc.*, 1930, 7, 481).

Benzoylphenylacetylene and Cyanoacetamide.

The ketone was prepared by the method of Nef ; it was a deep yellow heavy oil boiling between 190° and 200° at 15-18 mm. (yield about 60%).

3-*Cyano*-4:6-*diphenyl*-2-*pyridone* (IV, R=*Phenyl*).—The substance was obtained in an yield of about 75% by Michael's method. It was very sparingly soluble in all solvents excepting glacial acetic acid and pyridine ; crystallised from glacial acetic acid it melted at 320°,

and was identical with the dehydrogenated product of the Michael's condensation product from benzalacetophenone and cyanoacetamide. It was soluble in moderately dilute alkalis, but not so in concentrated solutions, on account of the sparing solubility of the sodium salt. On much dilution the solution became turbid owing to the hydrolysis of the salt. It gave no colouration with ferric chloride. With Knoevenagel's reagent (diethylamine or piperidine) an identical compound was obtained in an yield of about 40-50%. (Found: N, 10·08. $C_{18}H_{12}ON_2$ requires N, 10·30 per cent.).

The N-*methyl* derivative obtained as usual was no longer soluble in alkalis, neither did it give any colouration with ferric chloride. It was very soluble in all common organic solvents excepting petroleum ether; crystallised from rectified spirit it was obtained in small colourless prisms, m.p. 175°. (Found: N, 9·85. $C_{19}H_{14}ON_2$ requires N, 9·78 per cent.). An identical compound was obtained by condensing the ketone with cyanoacetmethylamide.

Hydrolysis of (IV): *Formation of* 4:6-*Diphenyl*-2-*hydroxypyridine* (V, R=*Phenyl*).—It was isolated by diluting the sulphuric acid solution (yield, 80%). On filtering and washing it free from acids it was crystallised from rectified spirit in fine yellowish-white needles, m.p. 208°. It was identified with other samples of the substance in hand. (Found: N, 5·63. $O_{17}H_{13}ON$ requires N, 5·66 per cent.).

p-*Toluylphenylacetylene and Cyanoacetamide.*

The ketone was prepared by the action of *p*-toluyl chloride on the sodium salt of phenylacetylene in an exactly similar way as in the previous case (yield, 60%). The *p*-toluyl chloride was prepared by the action of thionyl chloride on *p*-toluic acid (yield, 85-87%). *p*-Toluylphenylacetylene was obtained as a heavy yellow oil, b.p. 200-10°/15 mm. It solidfied on cooling and was very soluble in all organic solvents excepting petroleum ether, and crystallised from rectified spirit in large yellowish prisms, m.p. 72°. (Found: C, 86·98; H, 5·83. $C_{16}H_{12}O$ requires C, 87·27; H, 5·45 per cent.).

3-*Cyano*-4-*phenyl*-6-p-*tolyl*-2-*pyridone* (IV, R=p-*Tolyl*).—The mixture became intense red on mixing and sodiocyanoacetamide went into solution on shaking; soon afterwards the mixture set to a solid mass and the colour paled down to a faint pink. The sodium salt was separated, and the free product isolated therefrom as usual (yield, about 78%). Crystallised from glacial acetic acid it was obtained as cream-coloured prismatic needles, m.p. 268°.

It was identical with a specimen of the cyanopyridone obtained from benzal-*p*-methylacetophenone and cyanoacetamide as also with another sample obtained by condensing α-methoxy-ω-*p*-toluylstyrene with cyanoacetamide (Basu, *private communication*). It resembled its lower homologue in all its physical and chemical properties. (Found: N, 9·89. $C_{19}H_{14}ON_2$ requires N, 9·78 per cent.).

The N-*methyl* derivative obtained as usual, crystallised from methyl alcohol in colourless needles, m.p. 136-38°. (Found: N, 9·57. $C_{20}H_{16}ON_2$ requires N, 9·33 per cent.). It was identified with a sample obtained by condensing the ketone with cyanoacetmethylamide.

Hydrolysis of the Compound: *Formation of* 4-*Phenyl*-6-p-*tolyl*-2-*hydroxypyridine* (V, R=p-*Tolyl*).—The hydroxypyridine was obtained in an yield of about 80% when the above condensation product was hydrolysed with 75% sulphuric acid in the usual way. It resembled its lower homologue in all its properties, both physical and chemical. It crystallised from rectified spirit in fine yellowish needles, m.p. 228°. It was identified with a specimen from stock by the method of mixed melting points. (Found : N, 5·53. $C_{18}H_{15}ON$ requires N, 5·36 per cent.).

p-*Toluylphenylacetylene and Ethyl Malonate.*

Formation of Ethyl 4-*Phenyl*-6-p-*tolyl*-2-*pyrone*-3-*carboxylate*.—The condensation was carried out by the method of Kohler (*loc. cit.*) by adding a trace of sodium ethoxide to a hot alcoholic solution of equivalent quantities of the ketone and the ester. The product was isolated on the next day by acidulating with acetic acid (yield, about 70%). The mother-liquor gave some more impure product which was rejected. It had all the properties attributed to its lower homologue by Kohler. It crystallised from methyl alcohol in pale yellow needles, m.p. 85°. (Found: C, 75·29 ; H, 5·56. $C_{21}H_{18}O_4$ requires C, 75·45 ; H, 5·39 per cent.).

The free pyrone (4-*phenyl*-6-p-*tolyl*-2-*pyrone*) was directly obtained when the above ester was taken up with an excess of sodium ethoxide in alcoholic suspension, and left over till the red colour that first developed, completely disappeared (usually 3 to 4 days). Some of the pyrone separated and the rest could be isolated on dilution of the mother-liquor ; crystallised from alcohol it was obtained in thin flakes, m.p. 133°, (decomp.) (yield about 65%). (Found: C, 82·25 ; H, 5·61. $C_{18}H_{14}O_2$ requires C, 82·44 ; H, 5·34 per cent.).

p-Nitrobenzoylphenylacetylene and Cyanoacetamide.

p-Nitrobenzoylphenylacetylene was prepared by the action of *p*-nitrobenzoyl chloride on sodium phenylacetylene in the usual way. The chloride was prepared by treating *p*-nitrobenzoic acid with thionyl chloride. The ketone, a solid, separated out on the addition of water to the ethereal reaction mixture, and was moderately soluble in ether, alcohol and benzene. Crystallised from acetone it was obtained in light, golden-yellow flakes, m.p. 161-62°. (Found: N, 5·67. $C_{15}H_9O_3N$ requires N, 5·58 per cent.).

3-Cyano-4-phenyl-6-p-nitrophenyl-2-pyridone (IV, R=p-*Nitrophenyl*).—The mixture became red as usual and the condensation was over very soon, resulting in the fading out of the colour to pale brownish-yellow. The product was isolated as usual (yield about 75 %). It was very sparingly soluble in all other solvents excepting pyridine and glacial acetic acid. Crystallised from pyridine diluted with a few drops of alcohol it was obtained in small canary-yellow felty needles melting at 332-33°. It resembled the other members of the series in its properties. (Found: N, 13·20. $C_{18}H_{11}O_3N_3$ requires N, 13·25 per cent.).

The N-*methyl* derivative crystallised from a mixture of amyl alcohol and pyridine (equal volumes); m.p. 322-24°. (Found: N, 12·59. $C_{19}H_{13}O_3N_3$ requires N, 12·69 per cent.).

Hydrolysis of the above Cyanopyridone: Formation of 4-Phenyl-6-p-nitrophenyl-2-hydroxypyridine (V, R=p-*Nitrophenyl*).—The cyanopyridone was more resistant towards hydrolysis than the preceding analogous compounds. It could however be hydrolysed by 80% sulphuric acid or fuming hydrochloric acid in a sealed tube (at 180-200° for 6 to 8 hours). The hydrolysis product was soluble in alkalis and gave a characteristic brown coloration with ferric chloride and resembled the other hydroxypyridines in its properties. Crystallised from dilute acetic acid it was obtained in yellow needles that melted at 275-76°. (Found: N, 9·45. $C_{17}H_{12}O_3N_2$ requires N, 9·60 per cent.).

p-Nitrobenzoylphenylacetylene and Ethyl Malonate.

Formation of Ethyl 4-Phenyl-6-p-nitrophenyl-2-pyrone-3-carboxylate.—The condensation was carried out, and the product separated,

in the usual manner. It crystallised from alcohol in dull yellow needles, m.p. 148°. (Found: N, 4·01. $C_{20}H_{15}O_6N$ requires N, 3·84 per cent.). When hydrolysed with sodium methoxide in methyl alcoholic solution in the cold it gave rise to 4-*phenyl*-6-p-*nitrophenyl*-2-*pyrone*, that crystallised from acetic acid in light yellow needles and melted at 235°. (Found: N, 4·86. $C_{17}H_{11}O_4N$ requires N, 4·78 per cent.).

Acetylphenylacetylene and Cyanoacetamide.

The ketone, an yellow oil, b.p. 125-30°/ 15-18 mm., was obtained in about 25% yield.

3-*Cyano*-4-*phenyl*-6-*methyl*-2-*pyridone* (IV, R=*Methyl*).—That the reaction did not proceed very smoothly was evident from the fact that the reaction mixture became first red (as usual) and then instead of fading away (as recorded in the previous cases) became perceptibly brown as the reaction proceeded resulting in the separation of the sodium salt of the condensation product. It was, however, isolated as usual but the yield barely reached 40-50%. It resembled the other members of the series described, and crystallised from aqueous acetic acid in light yellow prismatic needles, m.p. 275-76°. An identical compound was also obtained when the condensation was carried out in the presence of Knoevenagel's reagents. The yield was very low, but was quite sufficient for the comparison. (Found: N, 13·58. $C_{13}H_{10}ON_2$ requires N, 13·33 per cent.). It was further identified with a specimen from stock, as obtained from benzalacetone and cyanoacetamide.

The N-*methyl* derivative crystallised from methyl alcohol in nearly colourless needles, m.p. 146°, and resembled the other members of the series. Sen's compound. (*vide supra*) also had an m.p. of 146°, and must have been identical with it. (Found: N, 12·73. $C_{14}H_{12}ON_2$ requires N, 12·50 per cent.).

Hydrolysis of the above Cyanopyridone: *Formation of* 4-*Phenyl*-6-*methyl*-2-*hydroxypyridine* (V, R=*Methyl*).—The compound was easily obtained by hydrolysing the original condensation product by 75% sulphuric acid (yield about 60%). It had all the properties of the hydroxypyridines described above. It was easily soluble in most solvents ; crystallised from rectified spirit it was obtained in fine needles, m.p. 206-8°. (Found: N, 7·78. $C_{12}H_{11}ON$ requires N, 7·57 per cent.).

Acetylphenylacetylene and Ethyl Malonate.

Formation of Ethyl 4-Phenyl-6-methyl-2-pyrone-3-carboxylate.—The condensation was carried out in the usual way. The substance, crystallised from methyl alcohol in pale yellow plates, m. p. 92°. (Found: C, 69·14; H, 5·51. $C_{15}H_{14}O_4$ requires C, 69·38; H, 5·42 per cent.). The ester when hydrolysed in the usual way gave rise to *4-phenyl-6-methyl-2-pyrone* which resembled the previously described pyrone derivatives from *p*-toluylphenylacetylene etc. in all its properties and crystallised from alcohol in thin pale yellow plates, m.p. 185-86°. (Found: C, 77·18; H, 5·25. $C_{12}H_{10}O_2$ requires C, 77·42; H, 5·38 per cent.).

Propionylphenylacetylene and Cyanoacetamide.

The ketone, prepared by the method of Moureau and Brachin, (*Compt. rend.*, 1903, **137**, 795), is an yellow oil boiling at 115-20°/15 mm. (yield about 28%).

3-Cyano-4-phenyl-6-ethyl-2-pyridone (IV, R=*Ethyl*).—The reaction proceeded in an exactly similar way to the preceding case (yield about 40%). It resembled the other members in all respects. Crystallised from aqueous acetic acid it was obtained in pale yellow prismatic needles, m.p. 267-68°, (Bardhan recorded 260°) sintering and darkening a few degrees earlier. It was identified with a specimen obtained from the condensation of cyanoacetamide and α-methoxy-ω-propionylstyrene (Basu, *private communication*). (Found: N, 12·32. $C_{14}H_{12}ON_2$ requires N, 12·50 per cent.). The same compound was also obtained when the condensation was carried out in the presence of diethylamine or piperidine.

The N-*methyl* derivative crystallised from methyl alcohol in fine needles, melting at 158°, and resembled the other methyl derivatives described before. (Found: N, 11·93. $C_{15}H_{14}ON_2$ requires N, 11·76 per cent.).

Hydrolysis.—*4-Phenyl-6-ethyl-2-hydroxypyridine* (V, R=*Ethyl*).—The cyanopyridone was easily hydrolysed by 75% sulphuric acid. The hydroxypyridine separated only on neutralising the solution with sodium carbonate. It was very soluble in all common solvents, and resembled the other members of the series. Crystallised from 40% alcohol it was obtained in colourless needles, m.p. 165°. It was identified with other specimens of the hydroxypyridine from

other sources (*q.v.*) (Found: N, 7·04. $C_{13}H_{13}ON$ requires N, 7·04 per cent.).

Further work with esters of unsaturated acids is in progress, and will be shortly communicated.

In conclusion, I desire to express my sincere thanks to Professor H. K. Sen, for his kind interest in this work and to Mr. U. Basu, for kindly providing me with several of his compounds for comparison. My thanks are also due to the Indian Chemical Society for a grant which has defrayed a part of the cost of chemicals used in the present work.

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A Study of Some Properties of Nitrocellulose made from Jute with Special Reference to its Stability.

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In view of the large output and economic importance of jute fibre, it would be interesting to investigate if this fibre could at least partly replace cotton or linter as a source of cellulose. In the following work some of the properties, particularly the stability, of jute nitrocellulose (*Corchorus capsularis*) have been studied and compared with those of cotton (*Gossypium herbaceum*).*

Nitrocellulose as prepared from jute fibre has been studied by Cross and Bevan (*J. Chem. Soc.*, 1880, **38**, 667; 1889, **55**, 202) and by Mühlhäuser (*Dingl. Polyt. J.*, 1882, **284**, 137). The former obtained an unstable product though it is not known whether they attempted to improve the stability while Mühlhäuser did not investigate the stability of his product. Owing to the technical importance of stability of nitrocelluloses, attempts have been made in these investigations to obtain a product from jute as stable as that from cotton and to get an idea of the ingredients which cause instability of jute nitrocellulose. It is satisfactory to note that nitrocellulose from jute has been made as stable as that from cotton though the fibrous structure was lost to a considerable degree during the process of stabilisation and the solution in ether-alcohol was found considerably less viscous than the corresponding solution of nitrated cotton. This is however an advantage for certain purposes, *e.g.*, for lacquer industry where low viscosity solutions are preferred.

In the course of stabilising the nitrocellulose, it has been found that continued boiling, particularly with acidulated water, degraded the product. Moderate acid-boiling must be followed by thorough washing with dilute alkali and water. The best stability results were however obtained by boiling with alcohol which dissolved the unstable sugar nitrates. Even the untreated raw fibre may thus be made to yield a very stable light-brown product, nitro-lignin being evidently dissolved by alcohol.

* Jute used in these experiments belonged to the variety known as *Bengal Kostha* and was obtained locally. Cotton used in these experiments was of 'Surat' type obtained through the courtesy of Dhakeswari Cotton Mills Ltd.

The different stability tests did not give identical results. The low temperature Abel test was found quite useful in detecting highly unstable products but was of little value when comparatively stable sugar-nitrates were present. For this purpose however the German 135° test was quite satisfactory, as most sugar-nitrates decomposed near about this temperature (Will and Lenze, *Ber.*, 1898, **31**, 68).

Nitration of Cotton and Jute.

Previous treatment.—For the purpose of nitration, cotton was purified by boiling with 1% caustic soda solution for one hour and the moisture content kept constant (0·5—1%). Jute was nitrated in different stages of purification. Whenever delignified fibre was used, it was prepared by chlorine peroxide method as cellulose and the accompanying carbohydrates are least affected by this reagent.

Procedure.—10 G. samples of purified and dried cellulose were nitrated in a large beaker by immersion in 500 g. acid mixture, the proportion of sulphuric acid, nitric acid and water being respectively as 61·2:21·2:17·6. This mixture was constantly stirred and nitration continued for 45 minutes during which time the maximum temperature attained was 32—35°, while the initial temperature of the bath ranged from 22 to 25°. The bulk of the acid was then removed by pressing the product on a perforated disc and the nitrocellulose suddenly immersed in a large volume of cold distilled water. Washing with cold water was then continued until the wash-water was neutral to litmus.

The following table shows some of the results obtained with jute and cotton nitrocelluloses. In the case of jute, the delignified fibre was purified to some extent by treatment with 5% caustic soda solution in the cold so that the cellulose and hemicelluloses would not be materially affected while the acid constituents would be largely removed.

TABLE I.

Properties and yield of nitrocelluloses from cotton and jute.

Cellulose.	Yield.	Solubility in ether-alcohol.	Rate of flow.	Nitrogen content.
Cotton ...	157%	98%	4 secs.	12%
Jute ...	139	95	0·5	12·05

It will be noted from the above table that the yield of nitrocellulose from jute is much smaller. This is partly due to mechanical loss during the process of washing when the nitrated fibre

crumbles to powder but mainly to the presence of considerable amount of γ-cellulose which give water-soluble nitro-compounds.

A mixture of ether and alcohol (55 : 45) has been used as solvent for determining solubility while viscosity has been determined at 20° in 1% ether-alcoholic solution. For this purpose the falling sphere viscometer of Gibson and Jacobs has been used, the sphere having a diameter of 1/16 inch and the column of solution having 1 cm. diameter and 20 cm. length. The considerably low viscosity in the case of jute may be due to either physical or chemical differences in the cellulose constituent of the fibres, as similar results have been obtained also with carefully purified jute cellulose. It is probable that the degree of polymerisation of jute cellulose is less or that its micells are shorter than those of cotton. The stability results (Table VI) are not apparently influenced by this difference. As has already been observed, this low viscosity is not without its technical advantage for certain purposes.

Attention may also be drawn to the lower solubility of jute nitrocellulose though its viscosity is lower and the nitrogen content identical. It is evident that owing to the presence of foreign matters, the product obtained from jute is less homogeneous than that from cotton, the percentage of nonnitrated or lower nitrated cellulose being greater.

That the nitration of jute is retarded by non-celluloses is evident from the nitrogen content of different nitrocelluloses obtained by nitrating jute fibre of different degrees of purity. This is brought out by the following table.

TABLE II.

Effect of impurities on nitration of cellulose.

Fibre.	Method of purification.	Nitrogen content.
Cotton	Boiled with 1% caustic soda.	12·0%
Jute	Treated thrice with 18% (cold) and once with 5% (hot) alkali.	12·1
,,	Treated once with 18% alkali.	11·85
,,	Delignified and treated several times with 5% cold alkali.	12·05
,,	Delignified and extracted with water and alcohol under pressure.	12·0
,,	Delignified and extracted with water and alcohol at atmospheric pressure.	11·9
,,	Delignified only. ...	11·3
,,	Boiled once with 0·5% alkali. ...	10·8

Stabilisation of Nitrocellulose.

After removal of any adhering acids by repeated washing with cold water, the samples of nitrated cellulose were given four sour boils with 1% hydrochloric acid, each of four hours' duration, followed by neutral boilings with distilled water, two or three alkali-boilings with 0·3% sodium carbonate and finally by repeated washing with boiling water. The scheme of washing and the corresponding stability figures by both the 76° Abel test and the 135° German test are shown in the following table.

TABLE III.

Stabilisation of nitrated α-cellulose from jute.

Nitrogen content = 11·85%. Period of boiling = 4 hours each.

No. of acid boilings.	No. of alkali boilings.	No. of water boilings.	Stability (in mins.) Abel test.	German test. Appearance of colour.	Complete colour.	Brown fumes.
4	—	—	6	3	—	—
4	—	8	12	15	25	35
4	2	6	12	20	30	45

It will be apparent from the above table that boiling with dilute alkali after preliminary acid boiling is favourable and gives better stability figures by the 135° German test, the number and period of boiling being the same. Sulphuric acid could not be detected in the wash after the first two acid boilings. Prolonged heating with acid had a deleterious effect, due probably to the formation of fresh unstable products. Boiling with 1 % hydrochloric acid alone even up to 100 hours could not render nitrocellulose at all stable. It was also found that the stability increased gradually on heating the sour-boiled nitrocellulose with water for increased periods of time. This was found useful in comparing stability of nitrocelluloses of different degrees of purity.

TABLE IV*a*.

Stabilisation of nitrocellulose from jute treated with 5% alkali.

Nitrogen content = 12·05%. Period of boiling = 4 hours each.

No. of acid boilings.	No. of water boilings.	Stability (in mins.) Abel test.	German test. Appearance of colour.	Complete colour.	Brown fumes.
4	3	12	5	10	—
4	6	15	15	20	35
4	9	—	20	25	35
4	12	—	25	35	45
4	14	—	25	35	60

TABLE IV*b*.

Stabilisation of cotton nitrocellulose.

Nitrogen content = 12·0%. Period of boiling = 4 hours each.

No. of acid boilings.	No. of water boilings.	Stability (in mins.) Abel test.	German test. Appearance of colour.	Complete colour.	Brown fumes.
4	3	15	3	5	—
4	6	30	10	15	15
4	9	—	20	25	30
4	12	—	25	30	40
4	14	—	25	30	50

The above tables bring out the fact that increase of stability is of the same order in the case of both cotton and jute cellulose-nitrates. The slightly higher result in the case of jute may be due to the fact that nitrated jute was transformed into very fine pulp during the process of washing and as a result, impurities were better removed in this case.

Relative Stability of Nitrocelluloses from Jute of different Degrees of Purity.

Before nitration, the original jute fibre was subjected to different chemical treatments for the removal of different types of impurities such as (1) fats, waxes and resins, (2) lignin, (3) hemicelluloses and (4) pectin matters. The following tables give the stability results of the different nitrated jute cellulose.

(a) Nitrocellulose from lignified fibre.

Raw jute from which woody tissues were removed mechanically, was cut into small pieces and boiled for one hour with 0·5% caustic soda to remove the greater parts of oils and allied impurities. The following are the analytical data of the fibre.

Moisture	...	1·0%	Lignin	...	12·2%
Ash	...	0·5%	Furfural	...	9·5%
Fats, etc.	...	traces.			

The nitrocellulose obtained from the above lignified fibre was coloured deep yellow even after repeated washing and its nitrogen content and yield were lower than those of the nitrates obtained from more purified jute cellulose.

TABLE Va.

Stabilisation of nitrocellulose from raw jute.

Nitrogen content = 10·8%. Period of acid boiling = 4 hrs. each.
Period of alkali and water boiling = 3 hrs. each.

			Stability (in mins.)			
				German test.		
No. of acid boilings.	No. of alkali boilings.	No. of water boilings.	Abel test.	Appearance of colour.	Complete colour.	Brown fumes.
4	—	—	6	—	—	—
4	—	8	25	20	35	60
4	2	6	25	20	40	75

In the above tests, copious fumes were not evolved even after 100 minutes, the figures stated above being only the approximate time when evolution of fumes was suspected. During alkali treatment, the colour of the product changed from yellow to brown and the fibres crumbled to powder though there was no appreciable change in nitrogen content.

(b) *Nitrocellulose from delignified fibre.*

Raw jute, after preliminary treatment with 0·5% caustic soda, was delignified by treatment with chlorine peroxide gas. The following are the analytical data.

Moisture	0·8%	Lignin	nil.
Ash	0·2%	Furfural	7·8%

TABLE Vb.

Stabilisation of nitrocellulose from delignified fibre.

Nitrogen content = 11·3%. Period of washing = 4 hours each.

		Stability (in mins.)			
			German test.		
No. of acid boilngs.	No. of water boilngs.	Abel test.	Appearance of colour.	Complete colour.	Brown fumes.
4	8	27	10	12	15

(c) *Nitrocellulose from delignified fibre extracted with water and alcohol.*

Delignified jute was treated with boiling water for five hours and then with alcohol under reflux for the same period, washed and dried before use. The analytical data are as follows.

Moisture	1·0%	Lignin	nil.
Furfural	6·5%	Uronic carbon dioxide ...	appreciable.

TABLE Vc.

Stabilisation of nitrocellulose from delignified and extracted fibre.

Nitrogen content = 11·9%. Period of boiling = 4 hrs. each.

		Stability (in mins.)			
			German test.		
No. of acid boilings.	No. of water boilings.	Abel test.	Appearance of colour.	Complete colour.	Brown fumes.
4	7	15	5	—	—

(d) Nitrocellulose from delignified fibre freed further from uronic acids.

Delignified jute was extracted with water under ordinary pressure and then with alcohol at 3 atmospheres pressure for two hours. It gave Furfural, 5·1 per cent. and Uronic carbon dioxide, nil.

TABLE Vd.

Stabilisation of nitrocellulose from delignified jute, extracted and freed from pectin.

Nitrogen content = 12%. Period of each washing = 4 hours.

No. of acid boilings.	No. of water boilings.	Stability (in mins.) Abel test.	German test. Appearance of colour.	Complete colour.	Brown fumes.
4	7	18	3	—	—
4	18	—	15	20	40

(e) Nitrocellulose from delignified jute treated with 5% alkali in the cold.

The delignified fibre was treated several times in the cold with twenty times its weight of 5% caustic soda, washed with water and dilute acetic acid. Its furfural content was 2·2% and the nitrogen content of the nitrated product was found to be 12·05%. The stability tests are shown in Table IV*a*.

(f) Nitrated α-cellulose of jute fibre.

α-Cellulose was prepared from jute in the usual manner by treatment with 18% alkali, the furfural content being 2·5%. Nitrogen content of the nitrated product was 11·85%. The stability results are shown in Table II.

(g) Nitrocellulose from purified α-cellulose of jute.

The α-cellulose, as prepared above from jute, was further treated with 5% boiling caustic soda for one hour. This treatment brought down the furfural content to the lowest figure of 1·1%.

TABLE Ve.

Stabilisation of nitrocellulose from purified α-cellulose.

Nitrogen content = 12·1%. Period of each boiling = 4 hours.

Stability (in mins.)					
			German test.		
No. of acid boilings.	No. of water boilings.	Abel test.	Appearance of colour.	Complete colour.	Brown fumes.
4	8	12	15	20	30

In the following table, the results of the previous tables are placed together in order to get an idea of the variation of stability with the nature of impurity in the cellulose.

TABLE VI.

Effect of impurities on stability.

Cellulose.	Nitrogen content.	Stability. No. of acid boilings.	No. of water boilings.	Abel test.	German test. App. of colour.	Complete colour.	Brown fumes.
1. Raw jute ...	10·8%	4	8	25	20	35	60
2. Delignified jute	11·3%	4	8	27	10	12	15
3. „ extracted with water and alcohol	11·9%	4	7	15	5	—	—
4. „ extracted further with alcohol under pressure	12·0%	4	7	18	3	—	—
5. Jute treated several times with 5% cold alkali	12·05%	4	9	—	20	25	
6. Jute treated once with 18% cold alkali	11·85%	4	8	12	15	25	
7. „ boiled further with 5% alkali	12·1%	4	8	12	15	20	30
8. Cotton boiled with 1% alkali.	12·0%	4	9	—	20	25	30

The conclusions from the above results are rather striking. The very high stability in the case of raw jute is due probably to lower nitration while delignified jute gives a less stable product with a higher nitrogen content. It is therefore evident that lignin does

not affect stability. With higher nitrogen content (samples 3 and 4), the stability of nitrocellulose is found to decrease to some extent, and attains a satisfactory figure only after prolonged boiling. Thus thirteen boilings were necessary to stabilise sample 4 (Table V*c*.) in a satisfactory manner. Attention may also be drawn to samples 3—8, where the nitrogen contents are practically the same but stability results are widely different. It is probable that in samples 3—4, alkali-soluble carbohydrates are present which on nitration give unstable sugar-nitrates requiring prolonged boiling for complete removal. When the alkali-soluble impurities are largely removed as in sample 5, the same extent of boiling (9) gives a fairly good result, a more satisfactory value being obtained when the number of boiling is increased to 14 (Table IV*a*). On further removing these impurities with 18% alkali (sample 6), the stability is found to decrease. This is more prominent in sample 7, which has been subjected to several treatments with concentrated alkali. High concentration of alkali evidently affects the stability of nitrocellulose due to the partial degradation of cellulose itself or to the formation of oxycellulose. The adverse effect of mercerisation on the stability of cotton nitrocellulose has long been reported (Marshall, "Explosives", p. 139). It is stated that 17 hot washings in the case of mercerised cotton did not give the same stability figure as seven washes in the case of standard cotton.

In practice, therefore, it is more advisable to treat delignified cellulose with cold alkali of moderate strength. It will be observed that the stability of nitrocellulose from jute treated with 5% cold alkali is almost identical by the German test, though the Abel test always gives a slightly higher result in the case of cotton nitrocellulose.

Stabilisation by Washing with Alcohol.

Since alcohol is invariably used in all nitrocellulose industries either as a solvent or as dehydrating and gelatinising agents, it was thought advisable to study the method of stabilisation with alcohol. It has been found that in all cases very high stability is attained by treatment with alcohol, provided the greater portion of combined sulphuric acid is previously removed by means of preliminary acid boiling. A large number of experiments were made; only the more important and typical results are shown in the following table.

TABLE VII.

Stabilisation of nitrocellulose by treatment with alcohol.

Nitrocellulose from—	No. of acid boilings (4 hrs. each).	Period of alcohol treatment (days).	Stability German test.	
			Coloration.	Fumes.
Cotton	4	—	5	15
,,	4	3	20	45
,,	—	3	10	15
Jute	2	—	5	10
,,	2	3	15	25
,,	4	—	5	15
,,	4	3	25	60
Cotton	2	—	10	15
,,	2	3	20	35
,,	4	3	35	75
Raw jute	4	—	5	10
,,	4	10 hrs. (extracted under reflux.)	40	75

It may be noted that highly coloured samples of nitrocellulose are left practically colourless by repeated hot extraction with alcohol. Since it is well-known that bleaching deteriorates all kinds of cellulose forming oxycellulose or causing decomposition, alcohol may be used for bleaching as well as for stabilising nitrated cellulose. The alcohol-soluble impurities however do not usually amount to more than 2% of the weight of nitrocellulose, being slightly greater in the case of jute than of cotton. The nitrogen content of alcohol-extracted nitrocellulose remained the same as before extraction and apart from the removal of undesirable impurities, no loss of nitrocellulose occurred. The nature of the alcohol extract is now under investigation.

Conclusions.

(1) By suitable methods of stabilisation, satisfactory stability may be obtained from jute nitrocellulose, whatever the nature of impurities, usually accompanying the fibre may be.

(2) The greater the impurities in jute cellulose, the more thorough must be the stabilisation of the nitrocellulose.

(3) Washing with acidulated water alone is not sufficient to stabilise jute nitrocellulose but should always be followed by alkaline or neutral washing.

(4) Alcohol has been found to be an excellent stabilising agent.

(5) Very small amounts of sugars or easily hydrolysable pentosans and hexosans (wood gum and hemicelluloses) will cause considerable instability.

(6) Cellulose degraded by the action of concentrated alkali will give unstable products.

(7) The more the impurities in the cellulose, the less will be the nitrogen content of the nitrocellulose made from it.

(8) Uniform nitration of jute is more difficult than that of cotton, unless impurities are carefully removed previously.

(9) Jute nitrocellulose is considerably less viscous than cotton in ether-alcoholic solution, which may be taken to indicate that the two celluloses are not quite identical.

The author wishes to express his indebtedness to Dr. J. K. Chaudhury for suggesting and guiding this work and to Prof. J. C. Ghosh for taking keen interest and affording facilities for carrying it out.

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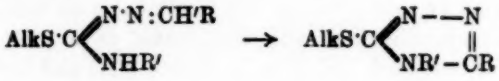
Studies on Oxidation. Part IV. Action of Ferric Chloride and Hydrogen Peroxide on *S*-Alkyl thiosemicarbazones: Formation of Triazoles.

By Satish Chandra De and Tarani Kanta Chakravorty.

In Part I of this series (De and Roy-Choudhury, *J. Indian Chem. Soc.*, 1928, **5**, 269) the oxidation of some thiosemicarbazones to thiodiazole or triazole derivatives has been described. In the present communication, the oxidation of *S*-alkyl thiosemicarbazones of aldehydes by means of ferric chloride and hydrogen peroxide is described. Since there are only two reactive hydrogen atoms in the molecule, and not three as in the case of an aldehyde thiosemicarbazone, the possibility of formation of thiodiazoles is totally excluded. The reaction therefore leads to triazoles irrespective of the nature of oxidising agents employed, which, in the case of aldehyde thiosemicarbazones, appear to have a selective action (Part I, p. 270).



The yields of the products, when ferric chloride was employed, were invariably poor, due evidently to the decomposition of the molecule. With *S*-alkyl benzylidenethiosemicarbazones no definite product could be separated. With hydrogen peroxide, the reaction proceeded smoothly and the yields were better. As the manipulative details are identical in both the cases, the oxidation with hydrogen peroxide only has been described in detail.

Experimental.

To an alcoholic solution of *S*-methylthiosemicarbazide hydriodide (Freund and Paradies, *Ber.*, 1901, **34**, 3114), the calculated amount of benzaldehyde was added and warmed. The condensation was followed by an immediate change of colour of the solution to yellow. The benzylidene derivative could not be isolated in a pure state.

5-Phenyl-3-methylthiol-1:2:4-triazole.—To the above solution, a little more than the calculated quantity of perhydrol diluted with ten times its volume of a mixture of alcohol and water (1:1) was added drop by drop through an upright condenser, with continuous shaking. The mixture was then boiled on the water-bath for about three minutes. The solution turned red and a tarry substance separated out. On passing steam through the mixture, the tar solidified; this was then repeatedly recrystallised from a mixture of alcohol and water (1:1) in white plates, m.p. 164°. (Found: C, 56·77 ; H, 4·89; N, 22·10. $C_9H_9N_3S$ requires C, 56·54 ; H, 4·71 ; N, 21·99 per cent.).

5-Phenyl-3-ethylthiol-1:2:4-triazole.—It was prepared in a similar way. Crystallised from dilute alcohol, it melted at 166°. (Found: N, 20·62. $C_{10}H_{11}N_3S$ requires N, 20·49 per cent.).

Benzylidene-S-methyl-4-phenylthiosemicarbazone.—A mixture of equimolecular quantities of 4-phenylthiosemicarbazide and methyl iodide was boiled in alcoholic solution for 15 minutes under reflux. One molecule of benzaldehyde was added and warmed. The deep yellow solution soon deposited pale yellow crystals which were recrystallised from rectified spirit, m.p. 153°. This is the hydriodide of benzylidene-*S*-methyl-4-phenylthiosemicarbazone, which is hydrolysed by boiling water. On treatment with moderately strong ammonia, the free base was precipitated as a pale yellow mass. This was collected, dried on a porous plate and crystallised from dilute alcohol, m.p. 66-67°. (Found: N, 15·59. $C_{15}H_{15}N_3S$ requires N, 15·61 per cent.).

The *hydrochloride* was obtained by shaking an absolute alcoholic solution of the substance with fuming hydrochloride acid.

4:5-Diphenyl-3-methylthiol-1:2:4-triazole.—An alcoholic solution of the above benzylidene-*S*-methyl-4-phenylthiosemicarbazone was treated with hydrogen peroxide as before. The mixture was boiled for 5 minutes and left overnight. Next day the crystals, which separated out along with a little tar, were collected pressed on a porous tile and twice crystallised from alcohol ; m. p. 165-66°. (Found: N, 16·00. $C_{15}H_{13}N_3S$ requires N, 15·73 per cent.).

The *hydriodide of benzylidene-S-ethyl-4-phenylthiosemicarbazone* was prepared in the same way as the methyl derivative and had m.p. 118°. The free base crystallised from alcohol and melted at 78°. (Found: N, 14·93. $C_{16}H_{17}N_3S$ requires N, 14·84 per cent.).

The *hydrochloride* crystallised from absolute alcohol and melted at 178° (decomp.).

4:5-*Diphenyl*-3-*ethylthiol*-1:2:4-*triazole*.—It was obtained by the oxidation of the above benzylidene compound, by means of perhydrol or ferric chloride. It crystallised from 50 per cent. alcohol as white needles, m.p. 148°. (Found: N, 15·07. $C_{15}H_{15}N_3S$ requires N, 14·95 per cent.). No tar was formed during oxidation with perhydrol.

Benzylidene-S-*methyl*-4-o-*tolylthiosemicarbazone*.— The hydriodide was prepared in the usual manner, and crystallised from rectified spirit; m.p. 189° (decomp.). The free base crystallised from alcohol, m.p. 62°. (Found: N, 14·95. $C_{16}H_{17}N_3S$ requires N, 14·84 per cent.).

The *hydrochloride* crystallised from absolute alcohol; m.p. 194° (decomp.).

4-o-*Tolyl*-5-*phenyl*-3-*methylthiol*-1:2:4-*triazole*.—After oxidation in the usual way by hydrogen peroxide or ferric chloride a dark coloured solution was obtained. No solid separated out during 3 days. Steam was then passed through the solution, when a semi-solid mass, which hardened on cooling was obtained. A small quantity of crystals was also obtained from the aqueous portion. These were crystallised from alcohol (charcoal) ; m.p. 130°. (Found: N, 15·08. $C_{16}H_{15}N_3S$ requires N, 14·95 per cent.).

4-o-*Tolyl*-5-*phenyl*-3-*ethylthiol*-1:2:4-*triazole*.—The hydriodide of benzylidene-*S*-ethylthiosemicarbazone, prepared in the usual way, crystallised from rectified spirit ; m. p. 123°. The free base was an oily substance which did not solidify. The *hydrochloride* melted at 167°.

Considerable quantities of tar were formed during oxidation, although it was conducted with great care. The crystals that came out from the aqueous portion were collected after a few hours and thrice crystallised from very dilute alcohol as silky needles, m. p. 107°. (Found: N, 14·33. $C_{17}H_{17}N_3S$ requires N, 14·24 per cent.).

Benzylidene-S-*methyl*-4-p-*tolylthiosemicarbazone*.— The hydriodide separated from rectified spirit; m.p. 180° (decomp.). The free base crystallised from alcohol; m. p. 71°. (Found: N, 14·96. $C_{16}H_{17}N_3S$ requires N, 14·84 per cent.). The *hydrochloride* melted at 130° (decomp.).

4-p-*Tolyl*-5-*phenyl*-3-*methylthiol*-1:2:4-*triazole*.—The free base was oxidised in the usual manner. On steaming the reaction products, the tar solidified. This was twice crystallised from dilute alcohol; m.p. 176°. (Found: N, 15·06. $C_{16}H_{15}N_3S$ requires N, 14·95 per cent.).

Benzylidene-S-*ethyl*-4-p-*tolylthiosemicarbazone*.—The hydroiodide crystallised from rectified spirit ; m.p. 165°. The free base was a semi-solid mass which did not solidify even on long standing. The hydrochloride crystallised from alcohol ; m.p. 158°.

4-p-*Tolyl*-5-*phenyl*-3-*ethylthiol*-1:2:4-*triazole*.— It formed silky white needles from alcohol; m. p. 148°. (Found: C, 68·79 ; H, 5·97 ; N, 14·54. $C_{17}H_{17}N_3S$ requires C, 69·15; H, 5·76; N, 14·24 per cent.).

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Reviews

Ausfuhrung quantitativer Analysen: (The Practice of Quantitative Analysis) by H. Biltz and W. Biltz with 49 figures. *Royal 8vo*, 400 pages. Published by Verlag von S. Hirzel in Leipzig C. 1, 1930.

This book gives instructions on quantitative analysis of inorganic substances. The introductory portion is devoted to the description of various manipulative analytical practices and other preliminary directions.

The book then deals with the gravimetric and volumetric estimation of individual elements discussing the theoretical principles underlying the different methods wherever it is necessary. Almost all the important recently developed methods of estimation as well as the electroanalytical methods and potentiometric titrations are included here.

The method of conductometric titration however is very summarily dealt with in a single page (p. 139) with general remarks without any details regarding the actual practice as applied to any concrete instance.

Then follows several chapters giving descriptions of processes for the analysis of various minerals, preparations, manures, pigments, alloys, steel, coal, coke, large varieties of ores foundry products, silicates including glasses. A short course of water analysis has also been included. These cover more than half the bulk of the book. The theoretical principles dealing with the methods of quantitative separation have been discussed in each individual case. One however misses here the minerals containing certain rarer elements like niobium, tantalum, beryllium, zirconium, thorium and the rare-earths. The addition of processes for the analysis of a few minerals like columbite, beryl, monazite, zircon, *etc.* would however have completed the course.

The descriptions of methods given in the book are lucid and condensed. Sources of probable error have also been indicated in each individual case. As most of the methods dealt with in this book have actually been tested in the authors' laboratories, the book

possesses a special importance of its own and will undoubtedly be of great practical help to the analytical workers. All unnecessary details, old and less reliable methods have been more or less excluded. A chapter on gas analysis which at present is wanting would have been welcome by many analysts.

One would however like to see the addition of some more improved methods of separation, *e.g.*, Lundell's method of separation of the ammonia group of elements from those of the ammonium sulphide group by ammonia in presence of an indicator, and also that based on the use of hexamine for the same purpose. These two recent methods have been found to possess decided advantages over the classical acetate method.

On the whole the book is a valuable addition to our existing standard text-books on analytical chemistry and can be commended as well to the beginners and advanced students as to the teachers on analytical chemistry. Tables of atomic weights, chemical factors and logarithms if annexed at the end would have been much appreciated by all workers. An English edition of the book will be welcome to the English speaking students and workers. The binding and printing of the book are quite good.

P. R.

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,,	557	,,	39	,, $C_{26}H_{32}O_2N_2$	,, $C_{26}H_{36}O_2N_2$
,,	561	,,	4	,, *p*-Imino-*d*-camphordiphenylamine.	,, *p*-Imino-*dl*-camphordiphenylamine.
,,	562	,,	31	,, *p*-amino-*d*-camphordiphenylamine.	,, *p*-amino-*dl*-camphordiphenylamine.
,,	563	,,	20	,, H, 7·82 per cent.	,, H, 7·69 per cent.
,,	571	,,	12	,, —544·0	,, —344·0
,,	573	,,	5	,, —540·7	,, —530·7

58°

The System, Water-Potassium Nitrate-Calcium Nitrate.

By Mohammed Abdul Hamid and Ram Das.

The investigation of the system, water-potassium nitrate-calcium nitrate, formed part of a larger work which was contemplated in connection with the refining of crude saltpetre (*J. Soc. Chem. Ind.*, 1916, **35**, 315T). This system has been worked out at 30° by Barbaudy (*Rec. trav. chim.*, 1923, **42**, 638-42). The isotherm of the system at 25° is shown in the accompanying figure and the data for this system at this temperature are given in the table.

For the determination of solubility, various complexes were vigorously stirred up to equilibrium in sealed tubes immersed in thermostats kept constant at 25° (±·1°). The potassium ion was determined by the cobaltinitrite method (Hamid, *Analyst*, 1926, **51**, 450) and calcium was precipitated as oxalate and weighed as oxide. The nitrate was determined by a modified method of Schlösing.

Table I.

Composition in g. per cent.				Solid phases.
Solution.		Wet residue.		
KNO_3	$Ca(NO_3)_2$	KNO_3	$Ca(NO_3)_2$	
27·30	0	—	—	KNO_3.
24·85	2·12	59·94	1·45	,,
23·83	4·96	64·09	2·17	,,
22·19	7·37	—	—	,,
21·53	11·48	61·21	5·32	,,
20·70	17·34	58·56	8·49	,,
20·32	19·14	—	—	,,
19·46	31·95	70·01	12·05	,,
19·22	40·34	70·20	15·12	,,
19·06	49·16	25·97	50·93	$KNO_3 + Ca(NO_3)_2$, $4H_2O$.
10·72	53·26	3·09	65·05	$Ca(NO_3)_2$, $4H_2O$.
7·37	54·82	1·00	67·92	,,
2·64	56·86	—	—	,,
0	57·98	—	—	,,

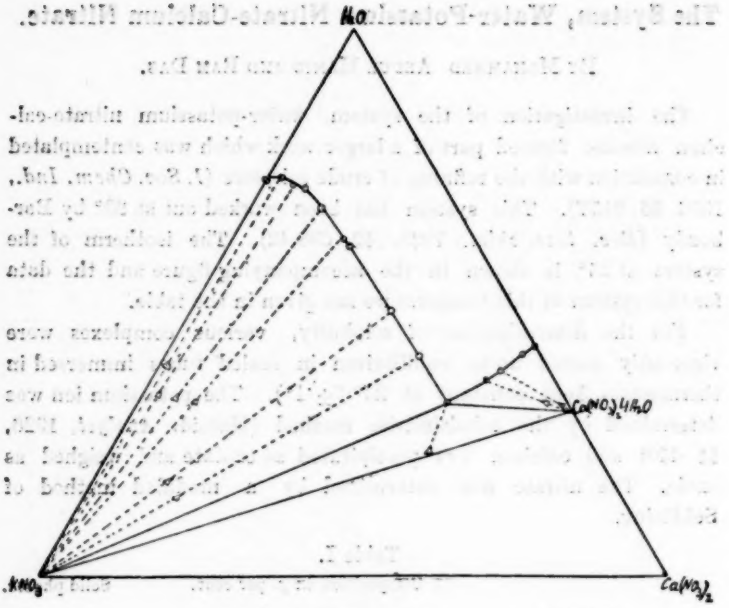

Fig. 1.

It has been observed that, with decreasing potassium nitrate concentration, the solution acquires a marked tendency to remain supersaturated for a considerable time. When an aqueous solution of calcium nitrate, saturated at the boiling temperature of water, is transferred to the thermostat in order to cool it to 25°, it first spontaneously deposits crystals, probably of the anhydrous salt or any of the lower hydrates, which redissolve on further cooling. The solution remains very viscous and crystallisation does not start for a long time. This difficulty was overcome by inoculating the solution cooled to 25° with a crystal of the tetrahydrate. At higher concentrations of potassium nitrate no such difficulty was experienced and the solution behaved in a perfectly normal way.

The authors are indebted to Dr. H. B. Dunnicliff for his kind help and interest in this work.

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Preparation of Electrolyte-Free Sol of Manganese Dioxide.

By Shridhar Sarvottam Joshi and T. Surya Narayan.

Gorgeu (*Ann. Chim. phys.*, 1862, **66**, 155), Spring and de Boeck (*Bull. Soc. chim.*, 1887, **48**, 170) obtained colloidal manganese dioxide in electrolyte-free condition by washing a freshly precipitated sample with conductivity water. The colloid-content of the sol was poor. The method adopted by most of the subsequent workers has been either the reduction of potassium permanganate or oxidation of a suitable manganese salt. This procedure introduces into the system appreciable traces of some electrolyte. Attempts at removing the electrolytes by dialysis result in the precipitation of the colloid on the dialysing septum. (*cf.* Cuy, *J. Phys. Chem.*, 1921, **25**, 415; Ganguly and Dhar, *ibid*, 1922, **26**, 701). The following experiments were carried out to obtain further information about this behaviour.

Experimental.

Fairly stable suspensions were obtained by (*i*) careful oxidation of manganese sulphate by bromine and (*ii*) reduction of permanganate by (*a*) formaldehyde, (*b*) ethyl acetate, (*c*) alcohol and similar agents. These methods were considered unsatisfactory, because of the residual electrolyte in (*i*) and possible formation of complex organic salts in (*ii*). The most satisfactory method was the reduction of potassium permanganate by concentrated ammonia, added drop by drop (Cuy, *loc. cit.*). Cataphoretic experiments showed that the sols were always negatively charged.

The sol used in the following experiments was prepared by the last method. In agreement with previous workers (*cf.* Cuy, *loc. cit.*), we found that the residual KOH had but little coagulating effect. Small amounts of even a moderately concentrated solution of KOH however precipitated the colloid. The sol coagulated slowly, when brought into contact with unglazed porcelain, animal charcoal, celluloid, glass-wool, filter and parchment papers. The course

of dialysis of the colloid with a negative potential applied to the dialysing septum was next investigated. The positive terminal of either the D. C. mains or of a battery of storage cells was earthed and the negative terminal was connected to a number of turns of platinum wire wound round the parchment sac, which was tied from one end of a well-cleaned glass tube and immersed in twice-distilled water. The volume of the sac was always greater than that of the sol, so as to avoid contact with the glass tube in view of the observed instabilising influence of glass. The results observed in one typical series of experiments are given below. These relate the magnitude of the negative potential with the time, during which a constant volume of the sol (10 c. c.) was observed to be stable in the dialyser.

Potential applied (volts).	0	6·5	10·5	24·0	52·0	220·0
Time (min.).	30	50	60	144	180	above 13 hrs.

It was found that after dialysing for about 13 hours, no sensible amount of KOH could be detected, when the sol after concentration to a very small volume by boiling, was tested with litmus. The possibility of the presence of free ammonia in the sol is excluded, as it would escape during boiling for concentration. Since in the preparation of the sol, ammonia was added drop by drop to a large excess of a boiling permanganate solution, and since the sol was further boiled before being stocked, and the alkalinity of the sol was perceptible only after concentration by boiling, any free ammonia could be present only in trace. Prolongation of the dialysis after the above stage induced a slow but sensible coagulation. We have found it possible to obviate this by use of still greater negative potentials. The resulting sol was much more sensitive to electrolytes.

Discussion.

It is seen that the stability of the colloid increases rapidly with applied potential. In an experiment, a positive potential of 200 volts was applied, and the whole colloid coagulated in about 10 minutes, as compared with 30 minutes with no potential applied.

The stabilising influence of the negative potential is apparently connected with the negative charge of the colloid, as its deposition on the dialyser would be to some extent counteracted by electric repulsion.

It was found that the same sol could be rendered electrolyte-free by hot dialysis. It follows therefore that the tendency of the sol to coagulate in ordinary dialysis cannot be appreciably due to any chemical interaction between the colloid and the dialyser material, since this would increase with temperature. It is known that coagulating tendency and adsorption are intimately connected, and that the latter diminishes with temperature. The increased stability of the colloid during hot dialysis may therefore be ascribed to the corresponding diminution in the adsorption of the colloid by the parchment. In hot dialysis, there is a possibility of peptisation (at any rate, contamination) of the colloid by traces of the dialyser material, disintegrated at the high temperature. Furthermore, factors like the size of the colloid particles, the stability of the sol might be affected during the process of hot dialysis. Evidence regarding this is afforded in the behaviour of the arsenious sulphide sol on heating (Kruyt and Spek, *Kolloid Z.*, 1919, **25**, 1; also, Mukherjee, *J. Chem. Soc.*, 1920, **117**, 350), and in the decomposing tendency of the uranium ferrocyanide sol under conditions of hot dialysis (Gore and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 648). None of these factors are present under the conditions of dialysis in the cold used here. Results of a detailed investigation, now in progress, examining the applicability of the present method to other colloids will be published in a later communication.

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Derivatives of Salicylic Acid. Part II. The 3-Nitro-5-sulpho- and 5-Nitro-3-sulpho-salicylic Acids.

By Andrew Norman Meldrum and Narhar Waman Hirve.

Following on the preparation of the 3- and 5-nitrosalicylic acids (*J. Indian Chem. Soc.*, 1928, **5**, 95), we proceeded to the preparation of the 3-nitro-5-sulpho- and 5-nitro-3-sulpho-salicylic acids. On examination of earlier work it appeared that, whatever the reason may be, these important acids had never been purified and analysed.

Two methods were thought of for the purpose: (*a*) sulphonation of the respective nitro-acids and (*b*) nitration of the respective sulpho-acids.

3-Nitro-5-sulphosalicylic Acid.

In attempting to sulphonate 3-nitrosalicylic acid, we used as agents (*a*) sulphuric acid and fuming sulphuric acid of different strengths and (*b*) chlorosulphonic acid, alone and in the presence of a catalytic agent (iodine, mercury, vanadium pentoxide) and we found that 3-nitrosalicylic acid resisted all our attempts. This is remarkable because the effect of the groups, -OH, $-NO_2$ and $-CO_2H$ in the 3-nitrosalicylic acid might each and all be expected to lead to the introduction of the sulphonic acid group in position 5 and remarkable, also, because the sulphonic acid in question is readily produced by nitration of 5-sulphosalicylic acid.

Hirsch (*Ber.*, 1900, **33**, 3240) treated 5-sulphosalicylic acid, with a mixture of nitric and sulphuric acids. Having obtained the crude acid in small amount, he prepared the barium salt, dehydrated this and analysed it. Sakellarios (*Ber.*, 1922, **55**, 2846) also used a mixture of nitric and sulphuric acids: he isolated only an acid potassium salt. Thus the acid has never been isolated in quantity and purified.

The isolation of the acid requires special attention to details. In trying Hirsch's method we found (*a*) that the use of fuming nitric acid (and sulphuric) gives dinitrosalicylic acid: (*b*) that 3-nitro-5-sulphosalicylic acid is readily soluble in sulphuric acid. Hirsch, in the hope of avoiding the production of dinitrosalicylic acid, used

sulphuric acid in quantity and for that reason obtained only a small amount of the desired acid. We find that when the amount of sulphuric acid is kept down the 3-nitro-5-sulphosalicylic acid separates in good yield: on crystallisation from water, it has the composition $C_7H_5O_8NS, 4H_2O$.

The following table shows the products that we obtained from salicylic acid (20 g.) under different conditions.

H_2SO_4.	HNO_3.	Sulphonitrosalicylic acid.	Dinitrosalicylic acid.	Sulphosalicylic acid.
153 g.	18 g.	Very little	Nil	10 g.
153 g.	18 g. (fuming)	Nil	28 g.	Nil
100 g.	21 g.	23 g.	Nil	Nil

The acid can also be obtained from 5-sulphosalicylic acid, using nitric acid dissolved in acetic anhydride. The solution is later poured into a solution of barium acetate when the orange salt $C_7H_3O_8NSBa, H_2O$ separates: from this the free acid can be obtained by using sulphuric acid and water.

*5-Nitro-3-sulphosalicylic Acid.**

Mandt (*Ber.*, 1877, **10**, 1701) heated 5-nitrosalicylic acid together with fuming sulphuric acid when 5-nitro-3-sulphosalicylic acid separated as a solid. He did not purify the acid and did nothing with it beyond preparing and analysing the salt $(C_7H_2O_8NS)_2Ba_3, 12H_2O$.

We have prepared 5-nitro-3-sulphosalicylic acid $C_7H_5O_8NS, 2H_2O$ by Mandt's method, and also his barium salt: although this salt is phenolic it is readily formed even in neutral solution because it is highly insoluble.

The Esters.

The two acids were converted into the methyl and ethyl esters $C_6H_2(NO_2)(OH)(SO_3H)CO_2R$: they were found to be stable substances that yield salts owing to the presence of the $-SO_3H$ and $-OH$ groups. The acids and the salts are remarkable in two ways: (1) they contain no water of crystallisation; (2) they are far weaker in colour than the original acids and their corresponding salts.

* The 5-nitrosulphosalicylic acid was not obtained from 3-sulphosalicylic acid by nitration because this acid was unknown: it has since been prepared by one of us (N. W. H.).

Experimental.

3-*Nitro-5-sulphosalicylic Acid.*

Method I.—Salicylic acid (20 g.) was dissolved in sulphuric acid (*d* 1·8, 100 g.): the solution was allowed to stand for an hour and 5-sulphosalicylic acid separated. The mixture was cooled below 20° and nitric acid (*d* 1·4, 21 g.) was added to it in small instalments while the mixture was kept cool. After the addition of all the nitric acid, and when the sulphonitro-acid began to separate the mixture was cooled in a refrigerator. The solid was collected and recrystallised from water as colourless glassy needles (yield, 23 g.). As it darkens if heated rapidly, water of crystallisation was determined by heating the acid under reduced pressure first at low temperature and then at 100°. (Found: H_2O, 21·29; N, 4·39; S, 9·66. $C_7H_5O_8NS$, $4H_2O$ requires H_2O, 21·50; N, 4·18; S, 9·56 per cent.).

Method II.—A mixture of nitric acid (*d* 1·4, 5 c.c.) and acetic anhydride (10 c.c.) was cooled; to it was added anhydrous sulphosalicylic acid (5 g.). After about six hours the mixture was poured into barium acetate solution when orange crystals separated out; they were collected and boiled with strong hydrochloric acid solution. The acid barium salt was formed, collected and recrystallised. The acid was liberated using the calculated amount of sulphuric acid and recrystallised from water (yield, 4·5 g.).

(1) The *acid barium salt* was prepared by digesting the neutral salt with concentrated hydrochloric acid. It easily changes to the neutral salt if heated with water, but can be safely recrystallised from acidic solution as parallelogramic plates of yellow colour. (Found: Ba 19·33; H_2O, 6·46. $(C_7H_4O_8NS)_2Ba$, $2\frac{1}{2}H_2O$ requires Ba, 19·44; H_2O, 6·37 per cent.).

(2) The *neutral barium salt* (orange) is difficultly soluble in water, and crystallises as long-plates: on losing water of crystallisation it turns yellow. (Found: Ba, 32·96; H_2O, 4·25. $C_7H_3O_8NSBa$, H_2O requires Ba, 32·99; H_2O, 4·32 per cent.).

Method III.—The method of Sakellarios (*loc. cit.*) was followed, that is, the nitration mixture was poured into a solution of potassium chloride (140 g. in 1400 c. c. water) except that the temperature was kept at 15-20° (Sakellarios, 30°). The salts that separated were a mixture of the acid potassium salt of 3-nitro-5-sulphosalicylic acid and the potassium salt of dinitrosalicylic acid. The salts were dissolved and the solution was neutralised by potassium carbonate.

The dipotassium salt of the 3-nitro-5-sulphosalicylic acid separated first and was found to be pure.

The *acid potassium salt* was prepared by acidifying the dipotassium salt, obtained above, with hydrochloric acid. It crystallises from water as long, pale yellow plates with a molecule of water of crystallisation. The anhydrous salt is white.

The *neutral potassium salt* was prepared as above. It is moderately soluble in hot water and crystallises as shining yellow plates. It contains water of crystallisation which could not be expelled even by heating at 100° under reduced pressure. (Found : K, 22·23. $C_7H_3O_8NSK_2$, H_2O requires K, 21·88 per cent.).

The *phenolic potassium salt* was prepared by adding strong potassium hydroxide to either of the above salts. It is easily soluble in water and crystallises as hexagonal prisms of reddish-yellow colour. (Found : H_2O, 4·60 ; K, 29·13. $C_7H_2O_8NSK_3$, H_2O requires H_2O, 4·56 ; K, 29·67 per cent.).

5-Nitro-3-sulphosalicylic Acid.

This was prepared by the method of Mandt (*loc. cit.*). 5-Nitrosalicylic acid (20 g.) was dissolved in fuming sulphuric acid (19 per cent. SO_3, 40 c. c.) and the solution was heated on the boiling water-bath for two and a half hours. When crystals began to separate, the mixture was cooled and the solid was collected on glass wool and crystallised from water: parallelogrammic plates (yield, 27 g.). The substance is deliquescent.

The crystals were dried by pressing them on a porous tile and then keeping them for a short time over calcium chloride in a desiccator. The acid was heated at 120° under reduced pressure in order to determine water of crystallisation. (Found: H_2O, 11·87 ; N, 4·71 ; S, 10·82. $C_7H_5O_8NS$, $2H_2O$ requires H_2O, 12·04 ; N, 4·68 ; S, 10·71 per cent.).

The *phenolic barium salt* $(C_7H_2O_8NS)_2\,Ba_3,12H_2O$ was prepared by Mandt. We obtained the salt and confirmed Mandt's formula. The salt is highly insoluble. Though it looks gelatinous under the microscope it is seen to consist of very small yellow needles.

The *neutral barim salt* was prepared by digesting Mandt's salt with strong hydrochloric acid. It is difficultly soluble in water from which it crystallises in white grains. (Found: Ba, 33·94. $C_7H_3O_8$-NSBa requires Ba, 34·48 per cent.).

The *phenolic potassium salt* was prepared by adding an excess of strong potassium hydroxide solution to the acid. It is easily

soluble in water and crystallises from it in yellow needles containing water of crystallisation. The anhydrous salt is crimson in colour. (Found, H_2O, 12·16 ; K, 27·33. $C_7H_2O_8NSK_3$, $3H_2O$ requires H_2O, 12·52 ; K, 27·18 per cent.).

The *neutral potassium salt* was prepared by neutralising the acid by potassium hydroxide solution. It is moderately soluble in water from which it crystallises as crimson needles. (Found: H_2O, 11·48 ; K, 19·96. $C_7H_3O_8NSK_2$, $2\frac{1}{2}H_2O$ requires H_2O, 11·72 ; K, 20·34 per cent.).

The *acid potassium salt* was prepared by adding potassium hydroxide solution to a solution of the sulphonic acid till a yellow tinge just appeared. It is difficultly soluble in water and crystallises as colourless white needles. (Found: K, 12·93. C_7H_4NSK requires K, 12·98 per cent.).

The *neutral silver salt* was prepared by adding silver nitrate to a solution of the ammonium salt. It is difficultly soluble in water, from which it crystallises as yellow plates. (Found : Ag, 44·91 ; $C_7H_3O_8NSAg_2$ requires Ag, 45·25 per cent.).

The Esters.—We converted each of the two acids into the methyl and ethyl esters, by the usual method. The esters separated from the reaction mixture as potassium salts, $C_6H_2(NO_2)(OH)(CO_2R)SO_3K$, on the addition of potassium chloride solution. They were converted into the barium salt $[C_6H_3N_3O(CO_2R)SO_3]_2Ba$ and then by means of sulphuric acid in the calculated amount into the ester. Each ester was recrystallised from a small amount of water. The esters are hygroscopic and very soluble in water and alcohol. The phenolic barium salts $[C_6H_2(NO_2)(CO_2R)SO_3]OBa$ are obtained on adding barium acetate solution to that of potassium salts. None of these substances, the esters, the potassium salts, and the barium salts contains water of crystallisation.

The following table shows the properties and composition of these substances:

Methyl 3-Nitro-5-sulphosalicylate.

Formula.	Appearance.	Solubility in water.	Found.	Required.
$C_8H_7O_9NS$	Slender needles.	Very soluble.	S, 12·08	S, 11·56 per cent.
$C_8H_6O_9NSK$	White silky needles	Difficultly soluble.	K, 12·21	K, 12·40 ,,
$(C_8H_6O_9NS)_2Ba$	Pale yellow needles.	Easily soluble at 100°.	Ba, 19·69	Ba, 19·92 ,,
$C_8H_6O_9NSBa$	Small yellow plates.	Difficultly soluble at 100°.	Ba, 33·34	Ba, 33·32 ,,

Ethyl 3-Nitro-5-sulphosalicylate.

Formula.	Appearance.	Solubility in water.	Found.	Required.
$C_9H_9O_8NS$	Long white needles.	Easily soluble	S, 10·89	S, 11·00 per cent.
$C_9H_8O_8NSK$	Pale white thin plates.	Difficultly soluble.	K, 11·73	K, 11·87 ,,
$(C_9H_8O_8NS)_2Ba$	Long pale yellow needles.	Easily soluble at 100°.	Ba, 18·81	Ba, 19·15 ,,
$C_9H_7O_8NSBa$	Microscopic yellow needles.	Difficultly soluble at 100°.	Ba, 31·99	Ba, 32·22 ,,

Methyl 5-Nitro-3-sulphosalicylate.

Formula.	Appearance.	Solubility in water.	Found.	Required.
$C_9H_7O_8NS$	Long white needles.	Easily soluble.	S, 11·86	S, 11·56 per cent.
$C_9H_6O_8NSK$	Rectangular white plates.	Difficultly soluble.	K, 12·26	K, 12·40 ,,
$(C_9H_6O_8NS)_2Ba$	Pale yeollw needles.	Soluble at 100°.	Ba, 19·67	Ba, 19·92 ,,
$C_9H_5O_8NS$ Ba	Pale yellow microscopic plates.	Difficultly soluble at 100°.	Ba, 33·42	Ba, 33·32 ,,

Ethyl 5-Nitro-3-sulphosalicylate.

Formula.	Appearance.	Solubility in water.	Found.	Required.
$C_9H_9O_8NS$	Long white needles.	Easily soluble.	S, 10·92	S, 11·00 per cent.
$C_9H_8O_8NSK$	Hexagonal plates.	Difficultly soluble.	K, 11·86	K, 11·87 ,,
$(C_9H_8O_8NS)_2Ba$	White needles.	Easily soluble at 100°.	Ba, 19·03	Ba, 19·15 ,,
$C_9H_7O_8NS$ Ba	Pale yellow grains.	Difficultly soluble at 100°.	Ba, 31·93	Ba, 32·22 ,,

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Derivatives of Salicylic Acid. Part III. 3-Sulphosalicylic Acid.

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On sulphonating salicylic acid one would expect to obtain 3- and 5-sulphosalicylic acids; but the former has never been described. The 5-sulpho-acid was obtained by (*a*) Mendius (*Annalen*, 1857, **103**, 45), by (*b*) Remsen (*Annalen*, 1875, **179**, 137), and by (*c*) Hirsch (*Ber.*, 1900, **33**, 3239). Remsen suspected the presence of another isomer in the mother-liquor. The suspicion was dismissed by Hirsch.

I have prepared 3-sulphosalicylic acid by sulphonating 5-nitrosalicylic acid and 5-aminosalicylic acid and then removing the superfluous group ($-NO_2$, $-NH_2$) in the usual way.

In order to avoid the suspicion that the sulphonic acid group may migrate during the removal of the superfluous group, a careful comparison was made of the 3-sulpho- and 5-sulpho-salicylic acids. The following table shows numerous points of difference between the properties and composition of the acids and their salts.

	3-Sulphosalicylic acid.	5-Sulphosalicylic acid.
Crystalline form ...	Silky needles.	Rectangular plates.
Solubility in sulphuric acid.	Easily soluble in cold.	Difficultly soluble in cold and hot.
Solubility in water ...	Easily soluble.	Less soluble than the isomer.
Composition ...	$C_7H_6O_6S$, $5H_2O$ and $C_7H_6O_6S$, $2H_2O$.	$C_7H_6O_6S$, $2H_2O$
Melting point ...	($C_7H_6O_6S$, $2H_2O$), 152°	Not definite.
Acid potassium salt ..	$C_7H_5O_6SK$; difficultly soluble.	$C_7H_5O_6SK$, $2H_2O$, easily soluble.
Barium salt ...	$C_7H_4O_6SBa$, $2H_2O$; difficultly soluble.	$C_7H_4O_6SBa$, $3H_2O$ easily soluble.

Further, when the 3-sulpho-acid was nitrated, the original 3-sulpho-5-nitrosalicylic acid was obtained; on bromination, 3-sulpho-5-bromosalicylic acid different from 5-sulpho-3-bromosalicylic acid was obtained. As this 3-sulpho-5-bromo-acid had not been described before, it was prepared also from 3-sulpho-5-aminosalicylic acid and was also converted by hydrolysis into the known 5-bromosalicylic acid.

Experimental.

5-Amino-3-sulphosalicylic Acid.

Method I.—5-Aminosalicylic acid (10 g.) was heated with fuming sulphuric acid (20% free SO_3 ; 20 c. c.) for about four hours. The sulpho-acid separated on cooling and the mother-liquor gave more of it on dilution with water. It is insoluble in alcohol, benzene and acetic acid. It is difficultly soluble in boiling water and crystallises as pale violet cubes with one molecule of water of crystallisation (yield, 15·5 g.). It decomposes at 353°. (Found: equivalent, 125·7; S, 13·30; N, 5·71 ; H_2O, 7·32. $C_7H_7O_6NS$, H_2O requires equivalent, 125·5 ; S, 12·77 ; N, 5·57; H_2O, 7·19 per cent.). If instead of boiling the solid with water, boiling water is poured on the solid, it goes into solution much more easily and on concentration of the solution it crystallises in long white needles with three molecules of water of crystallisation. These needles when heated with water are converted into the cubes. (Found: equivalent, 143·60; S, 11·23; N, 5·02; H_2O, 19·04. $C_7H_7O_6NS$, $3H_2O$ requires equivalent, 143·5 ; S, 11·14 ; N, 4·88 ; H_2O, 18·81 per cent.).

Method II.—5-Nitro-3-sulphosalicylic acid (10 g.) was dissolved in strong hydrochloric acid (40 c. c.) and iron * powder (in excess) was slowly added to it. Heat developed as the reaction proceeded and the 5-amino-3-sulphosalicylic acid separated on completion of the reaction. The solid was collected and crystallised from boiling water (yield, 8·5 g.).

The *neutral sodium salt* is easily soluble in water and crystallises from it in discoloured needles, with three molecules of water of crystallisation. (Found: Na, 14·14; H_2O, 16·15. $C_7H_5O_6NSNa_2$, $3H_2O$ requires Na, 13·90 ; H_2O, 16·31 per cent.).

The *neutral barium salt* is difficultly soluble in boiling water and separates as pale violet granules. (Found: Ba, 37·59. $C_7H_5O_6NSBa$ requires Ba, 37·29 per cent.).

5-Diazo-3-sulphosalicylic Acid.—5-Amino-3-sulphosalicylic acid (5 g.) was finely powdered and suspended in dilute hydrochloric acid (50 c.c.) and a solution of potassium nitrite (0·5 g.) was slowly added to it, keeping the temperature below 40°. The acid potassium salt of the diazosulphosalicylic acid separated. It was collected and

* Mandt (*Ber.*, 1877, 10, 1701) used tin. I find that tin soon becomes inactive when the sulphonic acid has not been carefully purified.

converted into the barium salt from which the diazo-compound was liberated. It is easily soluble in water and alcohol. It crystallises from water in reddish-yellow prismatic needles which decompose at 166° on heating rapidly and at 216° on slow heating (yield, 4·5 g.). (Found: equivalent, 122·1; N, 11·55. $C_7H_4O_6N_2S$ requires equivalent, 123·2; N, 11·48 per cent.).

The *acid potassium salt*, obtained as above, was crystallised from warm water. It formed shining pale yellow needles decomposing violently at 210°. (Found: K, 12·82; H_2O, 5·87. $C_7H_3O_6N_2SK$, H_2O requires K, 12·99; H_2O, 5·97 per cent.).

The *acid sodium salt* was obtained on diazotising the amino-sulpho-acid. It is easily soluble in water and was precipitated from the solution by addition of alcohol. It crystallises in pale shining yellow plates with half a molecule of water of crystallisation. It decomposes violently at 205°. (Found: equivalent, 274·0; Na, 8·11; H_2O, 3·15. $C_7H_3O_6SNa$, $\frac{1}{2}H_2O$, requires equivalent, 275·2; Na, 8·37; H_2O, 3·27 per cent.),

The *neutral sodium salt* is easily soluble in water and crystallises from it in red needles. (Found: Na, 15·91. $C_7H_2O_6N_2SNa_2$ requires Na, 16·00 per cent.).

The *neutral barium salt* is difficultly soluble in hot water and separates as yellow granules. (Found: Ba, 34·05; H_2O, 5·15. $C_7H_2O_6N_2SBa$, H_2O requires Ba, 34·58; H_2O, 4·53 per cent.).

3-*Sulphosalicylic Acid.*—The acid potassium salt of the 3-sulphosalicylic acid separated on refluxing the acid potassium salt of the diazo compound with a mixture of alcohol and water for about four hours. The disappearance of the azo-colour on coupling with alkaline β-naphthol indicated the completion of the reaction. The recrystallised acid potassium salt was converted into the barium salt from which the free acid was liberated in the usual way. It is easily soluble in water from which it crystallises in long needles having no definite m.p. It loses three out of five molecules of water on keeping overnight in a desiccator. This product has m.p. 152·5°. (Air-dried product: Found: equivalent, 153·6; H_2O, 32·32; S, 10·31. $C_7H_6O_6S$, $5H_2O$ requires equivalent, 153·67; H_2O, 31·73; S, 10·40 per cent. Desiccated product: Found: equivalent, 127·2; H_2O, 14·3; S, 12·4. $C_7H_6O_6S$, 2 H_2O requires equivalent, 127·07; H_2O, 14·19; S, 12·61 per cent.).

The *acid potassium salt* is difficultly soluble in boiling water from which it crystallises in tiny white needles. (Found: equivalent,

255·3; K, 15·12. $C_7H_5O_6SK$ requires equivalent, 255·5; K, 15·27 per cent.).

The *acid sodium salt* was prepared by a similar method to that for acid potassium salt. It is easily soluble in water and crystallises from it in needles. (Found: equivalent, 267·2; H_2O, 9·6; Na, 8·48. $C_7H_5O_6SNa$, $1\frac{1}{2}H_2O$ requires equivalent, 267·1; H_2O, 10·11; Na, 8·61 per cent.).

The *neutral barium salt* is very difficultly soluble in boiling water from which it crystallises in tiny white lustrous needles. (Found: Ba, 36·39; H_2O, 6·89. $C_7H_4O_6SBa$, $1\frac{1}{2}H_2O$ requires Ba, 36·11; H_2O, 7·10 per cent.).

5-Nitro-3-sulphosalicylic Acid.—The 5-nitro-3-sulphosalicylic acid obtained on nitration of 3-sulpho-salicylic acid ($C_7H_5O_8NS$, $2H_2O$) and its phenolic barium salt $(C_7H_2O_8NS)_2Ba$, $12H_2O$ had the properties and composition ascribed to them (*cf.* Meldrum and Hirve, preceding paper).

3-Sulpho-5-bromosalicylic Acid.

Method I.—The acid potassium salt of 3-sulphosalicylic acid (10 g.) was exactly neutralised with potassium hydroxide and bromine vapour (6 g.) mixed with air was then passed into it. The acid potassium salt of the sulpho-bromo-acid separated. It was collected and recrystallised and converted into the barium salt from which the acid was subsequently liberated. It is easily soluble in water and crystallises from it in long colourless silky needles, with four molecules. of water of crystallisation ; m. p. 98-100°. On keeping overnight in a desiccator it loses two molecules of water when it melts at 174° ; yield, 12·5 g. (Air dried substance: Found: equivalent, 185·8; H_2O, 19·43; S, 8·61 ; Br, 21·49. $C_7H_5O_6BrS$, $4H_2O$ requires equivalent, 184·6; H_2O, 19·51; S, 8·69; Br, 21·66 per cent.). Desiccated substance: Found: equivalent, 166·8 ; H_2O, 10·62; S, 9·53; Br, 23·92. $C_7H_5O_6$ BrS, $2H_2O$ requires equivalent, 166·5 ; H_2O, 10·81 ; S, 9·62; Br, 24·01 per cent.).

Method II.—3-Sulpho-5-diazo-acid-potassium-salicylate (3 g.) was dissolved in a mixture of hydrobromic acid (46 c. c. 18%) and water (20 c.c.), and cooled to room temperature. To this solution copper powder (5 g.) was added in small quantities, with shaking after each addition. A vigorous effervescence ensued. The reaction was completed by heating the mixture to boiling till the effervescence ceased. The mixture was filtered and the filtrate gave the acid

potassium salt of 3-sulpho-5-bromosalicylic acid: the acid when liberated was identical with that already described.

The *acid potassium salt* was recrystallised from water in needles. (Found: equivalent, 335·3; K, 11·49. $C_7H_4O_6BrS$ requires equivalent, 335·2; K, 11·65 per cent.).

5-Bromosalicylic acid was obtained by passing superheated steam through the solution of 3-sulpho-5-bromosalicylic acid for about four hours. It crystallises in silky white needles, m.p. 164°. (Hüber and Heinzerting, Z., 1871, 710 give 164°-165°; Lassar-Cohn and Schultze, *Ber.*, 1905, **38**, 3294 give 165°-166°). (Found: equivalent, 216·6. $C_7H_5O_3Br$ requires equivalent, 217·0).

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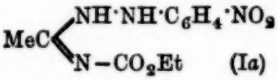
Synthesis of 1:2:4-Triazoles. Part I.

By Tejendra Nath Ghosh and Mangesh V. Betrabet.

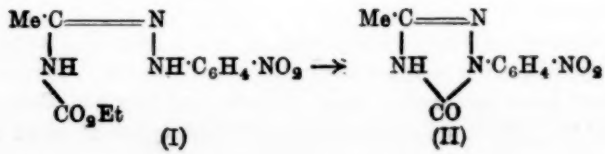
Andreocci (*Gazzetta*, 1889, **19**, 448) obtained an 1:2:4-triazole derivative by condensing phenylhydrazine with acetylurethane which bears a unique resemblance to acetoacetic ester. Using an aqueous solution of acetylurethane and phenylhydrazine hydrochloride in presence of sodium acetate, he obtained a mixture of an 1:2:4-triazole derivative and an oil which changed subsequently into a crystalline compound. He, however, did not study the latter compound in detail but assumed it to be the phenylhydrazone.

By condensing acetylurethane with other hydrazines according to the method of Andreocci, it has now been found difficult to separate the two constituents—more so because of the oily matter which is formed probably due to the decomposition of acetylurethane in aqueous solution. Hence it seemed advisable to study this sort of reactions under the influence of a condensing agent in an inert solvent. The conditions chosen for the reaction were similar to those of Rây and his co-workers (*J. Chem. Soc.*, 1926, **129**, 646; *J. Indian Chem. Soc.*, 1927, **4**, 541). When *p*-nitrophenylhydrazine and acetylurethane were condensed together, two products were isolated, one from the xylene solution and the other from the phosphoric acid residue by treatment with ice-cold water. The xylene-soluble product was found to be an amidine to which the constitution (I) has been assigned in preference to (I*a*) because of the fact that it does not form an azo-derivative on treatment with ferric chloride.



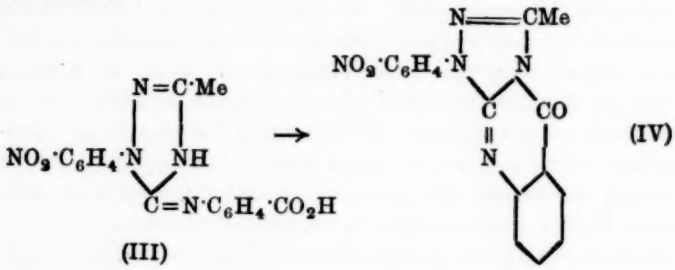
(I*a*)

The compound obtained from the phosphoric acid residue is an 1:2:4-triazole and is formed possibly from (I) by the elimination of a molecule of alcohol, thus:



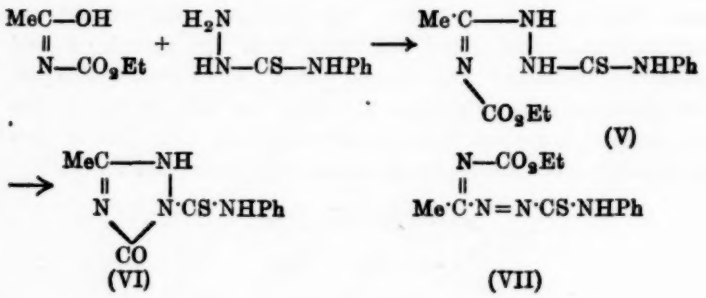
(I) (II)

To confirm the presence of the grouping (-NH-CO-) in (II) it was condensed with anthranilic acid in presence of phosphorus trichloride following the method of Sen and Rây (*loc. cit.*) when a mixture of 1-*p*-nitrophenyl-3-methyl-5-*o*-carboxyphenylimino-1:2:4-triazole (III) and 1-*p*-nitrophenyl-3-methyl-1:2:4-triazole-4:5-quinazolone (IV) was obtained.



(III) (IV)

Acetylurethane reacts with thiosemicarbazide and its substitution products to yield two compounds resembling those obtained from *p*-nitrophenylhydrazine, *viz.*, a hydrazoamidine the constitution of which was proved by the fact that it gave an azo-derivative (VII) on oxidation with ferric chloride (*cf.* Nef, *Annalen*, 1891, **266**, 70) and 1-phenylthiocarbamido-3-methyl-5-keto-1:2:4-triazole (VI).



(V) (VI) (VII)

From the condensation product of acetylurethane and thiosemicarbazide only the triazole derivative could be obtained (*vide* Experimental).

The condensation of acetylurethane was tried with phenols with the hope of getting morpholones in the same way as γ-pyrones are obtained from acetoacetic ester (Petsche and Simonis, *Ber.*, 1913, **46**, 2014). But in spite of the use of different types of condensing

agents under varying experimental conditions, the expected condensation could not be made to take place, although Rây and his coworkers (*loc. cit.*) could very easily condense acetylurethane with amines. This led us to believe that acetylurethane could condense with basic compounds only.

Experimental.

Preparation of Acetylurethane.—The method of Saloman and Kretzschmar (*J. pr. Chem.*, 1874, *ii*, **9**, 299) has been improved upon in this laboratory.* A mixture of equimolecular proportions of acetylchloride and urethane was heated under reflux at about 80° for about 20 minutes in a flask fitted with a calcium chloride tube and kept overnight. Next morning the colourless plates of acetylurethane were dried on a porous tile and crystallised from xylene; m.p. 77-78°. (Found: N, 10·52. $C_5H_9O_3N$ requires N, 10·68 per cent.).

Acetylurethane and p-*Nitrophenylhydrazine: Formation of Acetylurethane*-p-*nitrophenylhydrazone* (I) *and* 1-p-*Nitrophenyl*-3-*methyl*-5-*keto*-4:5-*dihydro*-1:2:4-*triazole* (II).—Acetylurethane (6·5 g.), *p*-nitrophenylhydrazine (7·5 g.) and xylene (30 c.c.) were heated with phosphoric oxide (20 g.) with stirring in an oil-bath at 125-130° for 2-3 hours. The reaction mixture was then allowed to cool. Xylene was decanted off from the sticky mass and furnished a reddish-brown crystalline product (I) on cooling, which further crystallised from acetic acid in reddish-brown prisms; m.p. 241° (yield 4 g.). (Found: N, 20·82. $C_{11}H_{14}O_4N_4$ requires N, 21·05 per cent.).

The sticky mass left in the flask was treated with ice-cold water and then with aqueous sodium hydroxide till the mixture became slightly acidic. The solid (II) that was obtained was crystallised from acetic acid in reddish-brown rectangular prisms, m.p. 259°. It is soluble in cold alkali and precipitated by acids (yield, 2·5 g.). (Found: N, 25·41. $C_9H_8O_3N_4$ requires N, 25·45 per cent.).

Condensation of Compound (II) *with Anthranilic Acid: Formation of* 1-p-*Nitrophenyl*-3-*methyl*-5-o-*carboxyphenylimino*-1:2:4-*triazole* (III) *and* 1-p-*Nitrophenyl*-3-*methyl*-1:2:4-*triazole*-4:5-*quinazolone* (IV).—A mixture of 1-*p*-nitrophenyl-3-methyl-5-keto-4:5-dihydro-1:2:4-triazole (4·5 g.), anthranilic acid (3 g.) and phosphorus trichloride (30 c.c.) was heated under reflux for 3—4 hours. The

* Mr. P. S. Mayuranathan has kindly permitted us to publish his method.

excess of phosphorus trichloride was then distilled off. The residue was treated with ice-cold water. The solid that was obtained was treated with dilute alkali when a portion went into solution. The alkaline solution was acidified with dilute hydrochloric acid when a solid (III) came down which crystallised from dilute acetic acid in pale brown prisms, m.p. 308°. It is acidic in nature and decomposes cold sodium bicarbonate (yield, 1 g.). (Found: N, 20·69. $C_{16}H_{13}O_4N_5$ requires N, 20·64 per cent.). The solid product (IV), insoluble in dilute alkali, was washed with water and crystallised from absolute alcohol in long brownish-yellow needles, m.p. 293° (yield, 2·5 g.). (Found: N, 21·86. $C_{16}H_{11}O_3N_5$ requires N, 21·80 per cent.).

Acetylurethane and Phenylhydrazine: Formation of Acetylurethanephenylhydrazone and 1-Phenyl-3-methyl-5-keto-4:5-dihydro-1:2:4-triazole.—A mixture of acetylurethane (2·5 g.), phenylhydrazine (2 g.) and phosphoric oxide (15 g.) in xylene (30 c.c.) was heated in the same way as in the case of the preceding compounds, when from the cold xylene solution colourless prisms separated out which was further recrystallised from alcohol; m.p. 142-143° (yield, 1·5 g.). (Found: N, 19·39. $C_{11}H_{15}O_2N_3$ requires N, 19·00 per cent.). From the sticky mass left in the flask after the removal of xylene and treatment with ice-cold water a reddish-brown substance was obtained which crystallised from alcohol in colourless prisms, m.p. 166-167° (yield, 0·5g.). (Found: N, 23·83. $C_9H_9ON_3$ requires N, 24·00 per cent.).

Acetylurethane and 4-Phenylthiosemicarbazide: Formation of 1-Phenylthiocarbamido-3-carbethoxyacetamidine (V) *and 1-Phenylthiocarbamido-3-methyl-5-keto-1:2:4-triazole* (VI).—An intimate mixture of acetylurethane (3 g.), 4-phenylthiosemicarbazide (4 g.) and phosphoric oxide (15 g.) in xylene (30 c.c.) was heated in an oil-bath at 125-130° for about 3 hours. Xylene was decanted off from the sticky mass and furnished a crystalline substance (V) on cooling, which further crystallised from alcohol in colourless prisms, m.p. 178°. (yield, 2·5 g.). (Found: N, 20·22; S, 11·23. $C_{12}H_{16}O_2N_4S$ requires N, 20·00; S, 11·42 per cent.). The residue from xylene after the usual treatment with water and sodium hydroxide yielded a solid product which crystallised from acetic acid in colourless rectangular plates (VI), m.p. 243° (yield, 1·5 g.). (Found: N, 23·62. $C_{10}H_{10}ON_4S$ requires N, 23·93 per cent.). It is insoluble in cold alkali and is desulphurised by treatment with yellow oxide of mercury.

The *azo-compound* (VII) was obtained by heating compound (V) with aqueous ferric chloride for about two hours when a red precipitate was obtained which crystallised from alcohol in brown

prisms, m.p. 225° (decomp.). (Found: N, 20·19. $C_{12}H_{14}O_2N_4S$ requires N, 20·14 per cent.).

Acetylurethane and 4-p-*Tolylthiosemicarbazide*: *Formation of* 1-p-*Tolylthiocarbamido*-3-*carbethoxyacetamidine and* 1-p-*Tolylthiocarbamido*-3-*methyl*-5-*keto*-1 :2 :4-*triazole*.—The method of procedure was similar to the preceding compounds (V and VI). The amidine obtained from xylene was crystallised from alcohol in colourless rhombic prisms, m.p. 203°. (Found: N, 18·94. $C_{13}H_{18}O_2N_4S$ requires N, 19·04 per cent.).

The triazole crystallised from acetic acid in colourless rectangular plates, m.p. 228°. (Found: N, 22·17. $C_{11}H_{12}ON_4S$ requires N, 22·58 per cent.).

Acetylurethane and 4-*Allylthiosemicarbazide*: *Formation of* 1-*Allylthiocarbamido*-3-*methyl*-5-*keto*-1 :2 :4-*triazole*.—The method of procedure was same. The xylene was decanted off and furnished a crystalline product which separated out from xylene in beautiful colourless plates, m.p. 201°. (Found: N, 28·05. $C_7H_{10}ON_4S$ requires N, 28·28 per cent.). (Yield 2 g. from 3 g. each of the reactants).

Acetylurethane and Thiosemicarbazide: *Formation of* 1-*Thiocarbamido*-3-*methyl*-5-*keto*-1 :2 :4-*triazole*.—An intimate mixture of acetylurethane (6 g.) and thiosemicarbazide (4 g.) in xylene (35 c.c.) was heated in an oil-bath at 130° with the addition of small quantities of phosphoric oxide from time to time for about 3 hours. The xylene was then decanted off and the solid residue left in the flask was treated with ice-cold water when phosphoric oxide went into solution and the condensation product remained as a precipitate which crystallised from dilute acetic acid in colourless prismatic needles, m.p. 222° (yield, 3·5 g.). (Found: N, 35·48 ; S, 20·13. $C_4H_6ON_4S$ requires N, 35·44; S, 20·25 per cent.). It is soluble in hot water, insoluble in alcohol and soluble in cold alkali. From the xylene solution, on evaporation, acetylurethane was recovered.

Our thanks are due to Professor P. C. Guha, D.Sc. and Dr. G. C. Chakravarti, D.Sc. for the kind interest they have taken in this work.

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Constitution of Corchorin—the Active Principle of Jute Seeds (*Corchorus Capsularis*). Part I.

By Nirmal Kumar Sen.

Corchorin, the active principle of jute seeds has been first isolated by the author in a very pure form by extracting *Corchorus capsularis* with alcohol. In a previous paper (*J. Indian Chem. Soc.*, 1930, 7, 83) an account was given of its chemical and physical properties and a short description of its pharmacological action. Although the amount of corchorin available did not permit of much information regarding its constitution, a number of interesting results have been obtained which are embodied in the present paper.

Corchorin is a bitter glucoside having the composition, $C_{22}H_{36}O_8$ which on hydrolysis yields one molecule of glucose and one molecule of corchogenin. Corchorin gives a crystalline pentacetyl derivative but the benzoyl derivative is an oil and could not be obtained in a crystalline condition.

Corchogenin, the sugar-free compound, has the composition $C_{16}H_{26}O_3$. The presence of a free carboxyl or alkyloxy-group in it could not be established in the usual manner but the presence of a lactonic grouping is shown by the results of the slow titration of its alcoholic solution with aqueous alkali hydroxide in presence of phenolphthalein, and hence its formula may be written as $(C_{15}H_{26}O)\begin{cases} CO \\ | \\ O \end{cases}$. It exhibits great stability towards the ordinary reagents.

An attempt to prepare an oxime as also a semicarbazone were unsuccessful. But it reacted on prolonged heating with phenylhydrazine forming an amorphous compound and with phosphorus pentachloride forming a chloro-derivative which also could not be obtained in a pure condition.

When corchogenin is brominated in chloroform solution a crystalline dibromide is produced showing the presence of a double bond in the molecule. By oxidation with potassium permanganate in the

* Read before the Indian Science Congress, Allahabad, January, 1930.

cold corchogenin yields corchoric acid having the composition $C_{15}H_{24}O_5$, while corchorin gives glucocorchoric acid which, on hydrolysis, gives corchoric acid and glucose.

Attempts were made to detect whether corchogenin contains any benzene or fused benzene nuclei by the application of the method of Ruzicka (*Helv. Chim. Acta*, 1921, **4**, 505); although hydrogen sulphide was evolved in quantity no trace of naphthalene hydrocarbon or simpler hydrocarbons could be isolated from the reaction products.

Corchogenin probably belongs to the homologous series having the general formula $C_nH_{2n-6}O_3$ (Abderhalden, "Biochemisches Hand Lexikon," Band 7, pp. 181, 187. Further work to elucidate the constitution of corchorin is in progress.

It may be further mentioned here that indication was obtained which led the author to suspect the presence of a second compound very similar in composition and property with corchorin in the mother-liquor from which the latter had been separated. A sufficient quantity of the mother-liquor is now being collected for further investigation which will form the subject matter of a subsequent communication.

Experimental.

Acetylcorchorin.—This compound was prepared by heating corchorin (1·1 g.) with acetic anhydride (12 c.c.) and pyridine (4 drops) under reflux for about two hours on a sand-bath, the solution being then poured in a thin stream into a large volume of water. A sticky matter separated which solidified on standing; it was collected, washed with water and dried. The acetyl compound crystallised from dilute alcohol (animal charcoal) slowly in colourless needles, m. p. 158° with decomposition. (Found: C, 60·35; H, 6·95 ; $CH_3.CO$ by Perkin's method, 32·4. $C_{22}H_{31}O_8(CH_3CO)_5$ requires C, 60·18; H, 7·21; CH_3CO, 33·69 per cent.).

It was very soluble in acetone, acetic acid and strong alcohol but insoluble in water. It gave a magenta colour with strong nitric acid.

Bromination of Corchorin: Monobromocorchorin Dibromide.—Corchorin (2 g.) dissolved in 40 c.c. of glacial acetic acid was treated with an excess of bromine dissolved in the same solvent. The mixture was allowed to stand at the ordinary temperature for about 4 hours and then warmed on the water-bath for half an hour. The excess of bromine and acetic acid were distilled off and the

residual liquid washed several times with a mixture of aqueous potassium iodide and sodium thiosulphate and finally with water. The product was then dissolved in a small quantity of glacial acetic acid and slowly poured into a large volume of water with constant stirring when a yellow solid was obtained. It was crystallised from dilute acetic acid in orange-red crystalline powder melting at 100° (decomp.). It had no bitter taste. (Found: Br, 35·68. $C_{22}H_{35}O_8Br_3$ requires Br, 35·9 per cent.).

On the addition of water to the mother-liquor a light yellow substance separated, which on fractional crystallisation from dilute acetic acid yielded another bromide melting at 146°. The quantity was too small for further investigation.

Hydrolysis of Corchorin: Corchogenin.—Corchorin (6 g.) was hydrolysed by heating with dilute sulphuric acid (400 c.c. of 10%) under reflux on a water-bath for 2 hours. The substance gradually went into solution giving a yellow opalescent solution. The resulting mixture when cold was extracted with ether and the ethereal solution washed several times until free from mineral acid, the ethereal solution being dried over anhydrous sodium sulphate and the ether evaporated off when a light yellow brittle substance wa obtained, which when crystallised from very dilute alcohol separated in glistening thin plates of irregular shape melting with decomposition at 112-114° (shrinks at 84°).

The aqueous acid-liquid was warmed to remove the ether and neutralised with excess of barium carbonate, filtered and evaporated to dryness; the residue was digested with absolute alcohol and the mixture filtered. On evaporating the alcoholic filtrate a small amount of a brown syrupy residue was obtained which reduced Fehling's solution, decolourised alkaline methylene blue solution at once in the cold and when heated gave the smell of burnt sugar. The syrup yielded an osazone melting and decomposing at 202°. It was thus evident that the sugar consisted of dextrose and the absence of ketose was proved by Pinoff's test (*Chem. Ztg.*, 1914, **38**, 629).

The hydrolysis of the glucoside took place in accordance with the equation,

$$C_{22}H_{36}O_8 + H_2O = C_{16}H_{26}O_3 + C_6H_{12}O_6.$$

The amount of glucose was estimated volumetrically with Benedict's solution (*J. Biol. Chem.*, 1911, **9**, 57). (Found: 41·61. Calc. 42·05 per cent.).

Corchogenin, the sugar-free compound, was found to be insoluble in water, sodium bicarbonate, sodium carbonate and in cold caustic soda but readily soluble in hot alkali and in almost all organic solvents and was sparingly soluble in acid solution. From its alkaline solution mineral acid precipitated a yellow amorphous mass which on warming with water was immediately changed into corchogenin. Its alcoholic solution was neutral to litmus. With concentrated sulphuric acid it dissolved with a reddish-brown colour and on addition of water a yellow substance (probably corchogenin) separated out. It did not reduce Fehling's solution but reduced hot ammoniacal silver nitrate and on prolonged heating reacted with phenylhydrazine giving an amorphous compound. With ferric chloride it gave an intense yellow colour in alcoholic solution and with acetic anhydride, chloroform and concentrated sulphuric acid it gave a blue colouration which rapidly changed to green. It decolourised bromine in chloroform and potassium permanganate in acetone solution. It burnt completely with a slightly sooty flame on a platinum foil leaving no residue. (Found: C, 71·85; H, 9·5; M. W. (cryoscopic in acetic acid), 250. $C_{16}H_{26}O_3$ requires C, 72·18; H, 9·77 per cent. M. W. 266).

Repeated attempts to acetylate and benzoylate corchogenin under different conditions were unsuccessful.

Action of Hydriodic Acid on Corchogenin.—When corchogenin (0·3152 g.) was heated with strong hydriodic acid (*d* 1·7) in a current of dry carbon dioxide according to the classical method of Zeisel as described by Benidict and Bamberger (*Montash.*, 1890, **11**, 260) and modified by Greger (*Montash.*, 1898, **19**, 116) there was no evidence of the presence of methoxy groups.

It was, however, noticed that a solid remained suspended in the acid after the treatment. This proved to be the unchanged material, the amount recovered being 0·095 g.

Bromination of Corchogenin: Corchogenin Dibromide.—The substance (2·1 g.) dissolved in chloroform (40 c.c.) was treated with an excess of bromine dissolved in the same solvent. The mixture was then heated under reflux for 3 hours. It was then treated in a manner similar to the preparation of bromocorchorin. When crystallised from dilute acetic acid it was obtained as a bright yellow crystalline powder, m.p. 130-32° (decomp.) (sintering at 110°). (Found: Br, 37·56. $C_{16}H_{26}O_3Br_2$ requires Br, 37·55 per cent.).

Action of Phenylhydrazine.—Corchogenin (0·3 g.) dissolved in glacial acetic acid was heated with a solution of phenylhydrazine acetate on the water-bath for about two hours. On cooling a yellow amorphous solid separated, m.p. 165-170° (decomp.). It contained nitrogen, but could not be obtained sufficiently pure for analysis.

Action of Phosphorus Pentachloride.—A mixture of corchogenin (1·13 g.) and excess of phosphorus pentachloride was heated for four hours on a water-bath. On cooling, the product—a dark red liquid—was poured into water and the precipitate collected and washed several times until free from acid. A dirty yellow product was obtained which could not be crystallised and melted at 120-125° with decomposition and charring. It was soluble in alcohol but slightly in benzene and petroleum ether. (Found: Cl, 33·9 per cent.).

Action of Soda Lime.—Corchogenin (0·6 g.) was mixed with soda lime and heated in a dry tube fitted with a delivery tube. Combustible fumes were given off and a sticky strongly-odoured solid condensed at the neck of the tube which in presence of chloroform absorbed bromine.

Action of Sulphur.—The dehydrogenation of corchogenin by heating it with excess of sulphur at 200-250° was carried out by Vesterberg's method (*Ber.*, 1903, **36**, 4200). There was a copious evolution of sulphuretted hydrogen and the melt was distilled at 12 mm. pressure. The dark coloured distillate was extracted with alcohol and on evaporation of alcohol a yellow, sweet-smelling oil was obtained which gradually darkened on exposure to air. The product was insufficient for purification, analysis and further studies.

Action of Alkaline Hydrogen Peroxide.—An alcoholic solution of corchogenin made alkaline with caustic potash was treated with hydrogen peroxide (Merck's perhydrol) with the addition of a little bromine as a starter. The action was vigorous and the solution gradually became colourless. After standing for some time it was acidified when nothing separated. It was then poured into water when a faintly yellow gelatinous mass separated out which was filtered. It contained bromine and when heated in a capillary tube it began to sinter at 82° and decompose with evolution of gas at about 128°. It was insoluble in caustic alkalis, sodium bicarbonate and on warming with caustic soda it resinified and turned yellow. Inspite of repeated attempts the substance could not be obtained sufficiently pure for analysis.

Oxidation of Corchorin: Glucocorchoric Acid.—Powdered potassium permanganate (6·8 g.) was added gradually to corchorin (5 g.) in ice-cold mechanically stirred acetone (250 c. c.), the colour of the permanganate disappeared slowly and the oxidation seemed to be complete after 24 hours. On reducing the manganese precipitate suspended in water with sulphurous acid a yellow turbid solution was obtained. This was repeatedly extracted with chloroform and the extract was washed with water and dried over anhydrous sodium sulphate. On evaporating the chloroform there remained a pale yellow solid which separated from alcohol in lustrous nacreous mass, m. p. 146-148°. It was soluble in hot water and in cold caustic soda and from the latter it could be re-precipitated by mineral acids; it slowly dissolved in sodium carbonate with the liberation of carbon dioxide. It dissolved in cold concentrated sulphuric acid with a faint yellow colour and did not reduce Fehling's solution. On heating with dilute hydrochloric acid it yielded an insoluble white product and the filtrate after neutralisation with soda readily reduced Fehling's solution. (0·2740g. neutralised 6·0 c. c. *N*/10-caustic potash. Neutralisation value, 122·86. Mean molecular weight, 456·6. (Found: C, 56·3; H, 7·5. $C_{21}H_{34}O_{10}$ required C, 56·5; H, 7·6 per cent. M. W., 446). On evaporating the acetone a further quantity of glucocorchoric acid was obtained. The yield of the acid was about 10 per cent.

Hydrolysis of Glucocorchoric Acid.—The substance was heated with dilute hydrochloric acid for one hour and the mixture on cooling was extracted with ether; the ethereal solution was washed until free from mineral acid, dried and the ether removed when a semi-solid substance having a characteristic smell separated out. On standing over concentrated sulphuric acid in vacuum it solidified and was crystallised from dilute alcohol in glistening plates, m. p. 67-70° and decomposing with evolution of gas at 94°. It was slightly soluble in water and the solution was acidic to litmus. It did not give any colouration with ferric chloride and dissolved readily in ammonia. From alcoholic solution an amorphous lead salt was precipitated by lead acetate. When heated on a platinum foil it first melted, charred and then burnt with a smoky flame leaving no residue. It slightly reduced Fehling's solution on prolonged heating but not ammoniacal silver nitrate solution. For this acid the name corchoric acid is proposed. (Found: C, 63·2; H, 8·6. $C_{15}H_{24}O_5$ requires C, 63·38; H, 8·45 per cent.).

There was not sufficient substance left to determine its molecular weight.

The aqueous acid-liquid was warmed on a water-bath and on neutralisation with sodium carbonate readily reduced Fehling's solution. It was t hen concentrated on a water-bath and warmed with sodium acetate and phenylhydrazine hydrochloride. Glucosazone, which separated very slowly, after being washed and dried, melted at 206°, alone or mixed with an authentic specimen.

It was afterwards found that the acid obtained by oxidising corchogenin with neutral potassium permanganate in the cold in a similar manner as in the case of glucocorchoric acid was identical with corchoric acid.

The author desires to thank the Indian Chemical Society for grants-in-aid of this work and to express his most sincere thanks to Professor S. N. Bose for his constant interest and inspiration. He also wishes to acknowledge his indebtedness to Prof. J. C. Ghosh and Dr. S. Dutt for their kind criticism.

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Potassium Chromate and Potassium Dichromate as Light-filters and the Constitution of Chromic Acid from Absorption Measurements.

By W. V. Bhagwat and N. R. Dhar.

The problem of obtaining suitable light-filters for isolating different spectral regions is in an unsatisfactory condition and our knowledge regarding the solution-filters appears to be meagre. The so-called monochromatic filters are seldom completely opaque to the other spectral regions. Quantitative investigation of filters is therefore of great importance in photochemistry.

In this communication, we have studied the absorption of potassium chromate and dichromate solutions of different concentrations in various regions of the visible spectrum. The use of solutions of potassium chromate in cutting off ultra-violet rays beyond 3660Å has been recommended. 0·001 Normal aqueous solution of potassium chromate in a quartz or uviol glass cell of 1 cm. thickness is said to absorb the mercury line 3660 Å. Wood (Physical Optics, 1914, p. 15) describes the use of potassium dichromate for the transmission of the green and the two yellow lines. No quantitative data, however, are available. A combination of cobalt glass and a saturated solution of potassium dichromate for the transmission of infra-red rays has been used. In a recent communication, Bhattacharya and Dhar (*J. Indian Chem. Soc.*, 1930, 7, 677) have shown that the filter consisting of a saturated solution of potassium dichromate in a cobalt-glass cell of 1 cm. thickness cuts off all visible and ultra-violet radiations and transmits infra-red radiations of wave-length 8500Å.

In the following tables are given our absorption measurements for both potassium chromate and dichromate in the different regions of visible spectrum. The absorption has been determined by a Hilger Nutting's spectro-photometer using a quartz cell of 1 cm. thickness. The results have been expressed as extinction coefficients. We have also calculated the percentage transmission in the various regions of the visible spectrum.

TABLE I.

Absorption measurements of Potassium chromate.

λ = wave-length in Å. ε = extinction coefficient.

(1) Concentration = 5·5 *N*.

λ	... 6700	6500	6200	5800	5600	5400	5350	5275
ε	... 0·08	0·08	0·08	0·08	0·08	0·28	0·48	0·61
λ	... 5200	5150	5000	4850	4600	4400	4299	4000
ε	... 1·68	∝	∝	∝	∞	∝	∝	∝

(2) Concentration = 2 *N*.

λ	... 6700	6500	6200	5800	5600	5400	5150
ε	... 0·08	0·08	0·08	0·08	0·08	0·26	1·04
λ	... 4950	4800	4600	4400	4200	4000	
ε	... ∝	∝	∝	∝	∝	∞	

(3) Concentration = *N*.

λ	... 6700	6500	6200	5800	5600	5400	5200
ε	... 0·08	0·08	0·08	0·08	0·08	0·19	0·26
λ	... 5150	5000	4950	4800	4600	4200	4000
ε	.. 0·44	0·61	∝	∝	∝	∝	∝

(4) Concentration = 0·1 *N*.

λ	... 6700	6500	6200	5800	5600	5400	5150
ε	... 0·07	0·07	0·07	0·07	0·07	0·07	0·08
λ	... 4950	4800	4600	4400	4200	4000	
ε	... 0·35	1·10	∝	∝	∝	∝	

(5) Concentration = 0·01 *N*.

λ	... 6700	6500	6200	5800	5600	5400	5150
ε	... 0·06	0·06	0·06	0·06	0·06	0·06	0·06
λ	... 4950	4800	4600	4450	4300	42·0	4000
ε	... 0·06	0·38	0·58	0·88	∝	∝	∝

(6) Concentration = 0·001 *N*.

λ	... 6700	6500	6200	5800	5600	5400	5150
ε	... 0·06	0·06	0·06	0·06	0·06	0·06	0·06
λ	... 4950	4800	4600	4400	4200	4000	
ε	... 0·06	0·12	0·16	0·26	—	—	

It will be observed from these results that with increasing concentration of potassium chromate, the absorption increases towards higher wave-lengths. For the saturated solution of potassium chromate (5·5 *N*) there is complete absorption for the wave-lengths shorter than 5150Å, while for greater wave-lengths, there is very little absorption. Thus there is sharp line of division between absorbed and transmitted part of the spectrum. This makes potassium chromate a very suitable light-filter, although its transmission range is large, extending from 5150-7000Å for visible region. But for whatever part it is transmitting, it practically causes no loss of intensity and this is highly advantageous from the viewpoint of a suitable filter. It has been observed by us that the combination of a saturated solution of K_2CrO_4 with cobalt glass behaves practically in the same way as the combination of cobalt glass with the saturated solution of potassium dichromate, which transmits only infra-red. Cobalt glass has high absorption for all the wave-lengths, longer than blue and is nowhere completely transparent for shorter wave-lengths. By using the glass of suitable thickness (about 0·5 cm.) practically all wave-lengths longer than blue are absorbed completely, and because the saturated solutions of both potassium chromate and dichromate have complete absorption for the wave-lengths shorter than blue and also for ultra-violet, the combination of cobalt glass either with potassium chromate or dichromate offers itself as a suitable filter for infra-red radiations. For the concentrations 2 *N*, *N*, 0·1*N*, 0·01*N* and 0·001 *N*, the regions shorter than 4950Å, 4950Å, 4600Å, 4300Å, 4000Å respectively are completely absorbed. Hence these concentrations can be used for the transmission of wave-lengths greater than those mentioned above. In all the cases the ultra-violet region is completely cut off. When the total visible spectrum is desirable, the use of potassium chromate of concentration 0·001 *N* is advisable. Thus the following results are obtained.

TABLE II.

K_2CrO_4 saturated + cobalt glass (0·5 cm. thick)	—	transmits infra-red radiations
Saturated solution of K_2CrO_4	—	cuts off wave-lengths shorter than 5150Å.
2 *N* solution of K_2CrO_4	do	4950Å.
N solution of K_2CrO_4	do	4950Å.
0·1 *N* solution of K_2CrO_4	do	4600Å
0·01 *N* solution of K_2CrO_4	do	4300Å.
0·001 *N* solution of K_2CrO_4	do	4000Å.

TABLE III.

λ = wave-length in Å. ϵ = extinction coefficient.

Absorption measurements of Potassium dichromate.

(1) Concentration 1·17 *N* (saturated solution at 34°).

λ ...	6700	6500	6200	5800	5750	5675	5600
ϵ ...	0·18	0·18	0·20	0·38	0·56	1·06	2·40
λ ...	5500	5200	4800	4600	4400	4200	4000
ϵ ...	∞	∞	∞	∞	∞	∞	∞

(2) Concentration = 0·1 *N*.

λ ...	6700	6500	6200	5800	5600	5400	5300
ϵ ...	0·08	0·08	0·08	0·12	0·20	1·20	2·02
λ ...	5275	5250	5200	4800	4600	4400	4000
ϵ ...	2·22	3·72	∞	∞	∞	∞	∞

(3) Concentration = 0·01 *N*.

λ ...	6700	6500	6200	5800	5600	5400	5100
ϵ ...	0·07	0·08	0·09	0·10	0·12	0·16	0·53
λ ...	4950	4750	4650	4600	4400	4200	4000
ϵ ...	0·99	1·42	2·14	∞	∞	∞	∞

(4) Concentration = 0·001 *N*.

λ ...	6700	6500	6200	5800	5600	5400	5100
ϵ ...	0·03	0·03	0·03	0·03	0·04	0·05	0·08
λ ...	4950	4800	4600	4450	4300	4150	4000
ϵ ...	0·12	0·16	0·20	0·27	0·28	—	—

It will be observed that a saturated solution of potassium dichromate absorbs completely all the wave-lengths shorter than 5600 Å. Thus the filter (conc. 1·17 *N*) is useful when only the rays of wave-length greater than 5600 Å are to be used. The concentrations 0·1 *N*, 0·01*N* and 0·001 *N* of potassium chromate absorb completely the wave-lengths shorter than 5200Å, 4600Å and 4000Å respectively. Hence when the rays of wave-lengths greater than those mentioned above are to be transmitted, the given concentrations of the solution of potassium dichromate will be found convenient.

TABLE IV.

Filter.	Radiations absorbed.
$K_2Cr_2O_7$ saturated + cobalt glass (0·5 cm. thick).	Visible and ultra-violet.
Normal solution of $K_2Cr_2O_7$	Shorter than 5600 Å
0·1 *N* ,,	,, 5200 Å
0·01 *N* ,,	,, 4600 Å
0·001 *N* ,,	,, 4000 Å

For the same concentration, potassium dichromate has a higher absorption than potassium chromate. This will be evident from the comparative table given below.

TABLE V.

Concentration.	Region of complete absorption.	
	K_2CrO_4	$K_2Cr_2O_7$
5·5 *N*	5150 Å	—
2 *N*	4950 Å	—
1·0 *N*	4950 Å	5600 Å
0·1 *N*	4600 Å	5200 Å
0·01 *N*	4300 Å	4600 Å
0·001 *N*	4000 Å	4000 Å

The maximum absorption obtained in the case of K_2CrO_4 is up to the limit of 5150 Å only, while it extends as far as 5600Å in case of $K_2Cr_2O_7$. Thus the filter $K_2Cr_2O_7$ is more useful than K_2CrO_4 for cutting off the major part of the visible spectrum especially beyond yellow. But it has the disadvantage over potassium chromate in that it has a much higher absorption in larger wavelengths than potassium chromate. Thus the intensity of the transmitted light is diminished to a greater extent than with K_2CrO_4 solution of the same concentration.

Hantzsch (*Z. physikal Chem.*, 1910, **72**, 362) has also determined the molecular extinction coefficient of solutions of potassium chromate and dichromate for 5460Å, 4860Å and 4360Å. His results show that the molecular extinction coefficients decrease slightly on dilution of the salts, whilst our measurements show that the molecular extinction coefficients increase markedly with dilution. We

have obtained similar results with several cupric salts, which also do not obey Beer's law. Moreover, the details of the experimental procedure of Hantzsch are not recorded in his paper and hence it is impossible to explain the discrepancy between his and our results. We have repeated our measurements and we have observed that our results are reproducible.

We now proceed to determine the percentage transmission of light in various regions of visible spectrum for aqueous solutions of different concentrations of potassium chromate and potassium dichromate. We have used a quartz cell 1 cm. thick. According to Lambert's law, the fraction of the incident light, which is absorbed by a medium of a definite thickness is independent of the initial intensity. According to this law, the absorption increases in geometrical progression as the thickness increases in arithmetical progression. Consider an absorbing medium of thickness l and let I_x be the intensity of the light after its passage through the length x of the medium. The decrease in intensity on passing through a thin layer dx of the medium is given by the expression

$$-dI = kI_x dl \qquad \ldots \quad (i)$$

where k is generally designated as the constant or coefficient of absorption. On integration we get

$$I = I_o e^{-kl},$$

or

$$\log \frac{I}{I_o} = -kl \qquad \ldots\ldots\ldots\ldots (ii)$$

where I represents the intensity of the emergent light. These results can be written in the form

$$I = I_o \ 10^{-El},$$

where E is the extinction coefficient. Hence percentage transmission is given by

$$\frac{100 \times I}{I_o} = \frac{1}{10^{El}} \times 100;$$

but in our case $l = 1$ cm. Therefore percentage transmission is given by

$$\frac{1}{10^{E}} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots (iii)$$

This is the relation that we have used in determining the percentage transmission of the solutions of potassium chromate and dichromate.

TABLE VI.

Percentage transmission of K_2CrO_4.

λ (Å)	Concentrations: 5·5 *N*	2·0 *N*	1·0 *N*	0·1 *N*	0·01 *N*	0·001 *N*
4000	0	0	0	0	0	—
4200	0	0	0	0	0	—
4400	0	0	0	0	13·0	54·9
4600	0	0	0	0	26·9	69·1
4800	0	0	0	7·9	41·7	75·8
4950	0	0	0	44·6	87·1	87·1
5150	0	9·1	54·9	83·1	87·1	87·1
5400	52·4	55·0	64·5	85·1	87·1	87·1
5600	83·1	83·1	83·1	85·1	87·1	87·1
5800	83·1	83·1	83·1	85·1	87·1	87·1
6200	83·1	83·1	83·1	85·1	87·1	87·1
6500	83·1	83·1	83·1	85·1	87·1	87·1
6700	83·1	83·1	83·1	85·1	87·1	87·1

TABLE VII.

Percentage transmission of $K_2Cr_2O_7$.

λ (Å)	Concentrations: 1·17 *N*	0·1 *N*	0·01 *N*	0·001 *N*
4000	0	0	0	—
4200	0	0	0	—
4400	0	0	0	53·7
4600	0	0	0	63·1
4800	0	0	3·8	69·1
4950	0	0	10·2	75·8
5150	0	0	30·2	83·1
5225	0	0	—	—
5300	0	0·95	—	—
5400	0	6·3	69·1	89·1
5550	0	—	—	—
5600	0·39	63·1	75·8	91·2
5675	8·7	—	—	—
5800	41·6	75·8	79·4	93·3
6200	63·1	83·1	81·2	93·3
6500	66·0	83·1	83·1	93·3
6700	66·0	83·1	85·1	93·3

It has been shown by Dhar (*Z. anorg. Chem.*, 1921, **121**, 99; *J. Indian Chem. Soc.*, 1928, **5**, 585) and by Bhagwat and Dhar (*J. Indian Chem. Soc.*, 1929, **6**, 781) that chromic acid exists mainly as H_2CrO_4 and potasium dichromate exists in solution chiefly as $KHCrO_4$ in dilute solutions. We have drawn the curves representing absorption of radiations of definite wave-lengths at different concentrations for both potassium chromate and dichromate. It has been observed that for high concentrations, the nature of the curves is widely different but as the concentration falls, the similarity of the curves is marked. Hence it appears that in very dilute solutions both chromate and dichromate behave similarly and hence chromic acid mainly exists as H_2CrO_4 in dilute solutions. Moreover it will be clear from the absorption data that Beer's law is not applicable. Beer's law is a molecular characteristic and appears to be valid for all solutions in which the molecular species undergo no fundamental change on dilution. In other words, as long as the molecular constitution is unchanged, absorption must be proportional to dilution. But this is not at all true for both the solutions of potassium chromate and dichromate. Inspite of the change of concentration from 1·0 *N* to 0·001*N*, there is practically the same absorption for high wave-lengths of visible spectrum. The explanation as to the formation of hydrated molecules of the type H_2CrO_4, $n\ H_2O$ or $H_2Cr_2O_7$, $n\ H_2O$, thus decreasing the actual water-content and increasing the concentration of the solution, appears unsatisfactory, when we consider the consistency of absorption results for such a wide range of concentration as 1·0 *N*−0·001 *N*. It is, therefore, clear that with the change of concentration, there is actually change in the molecular species. We are of the opinion that in concentrated solutions, there is an equilibrium of the type

$$H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$$

and this equilibrium shifts to the side of H_2CrO_4 on dilution. The colour of the saturated solution of potassium dichromate is red, which on dilution becomes orange and finally yellow, that is, it assumes the colour of the chromate. A saturated solution of potassium chromate has an orange tinge. It appears, therefore, that concentrated solutions of chromic acid and dichromates, may contain Cr_2O_7'' and HCr_2O_7' ions but in dilute solutions $HCrO_4'$ and CrO_4'' ions predominate.

Summary.

(1) The absorption and percentage transmission for aqueous solutions of potassium chromate and potassium dichromate of various concentrations have been determined. It has been observed that a saturated solution of potassium chromate (5·5 *N*) transmits wave-lengths longer than 5150Å. A saturated solution of potassium dichromate can conveniently be used to cut off all the wave-lengths shorter than 5600Å.

(2) In very dilute solutions, chromates and dichromates of potassium behave similarly, from the viewpoint of light absorption and hence chromic acid in dilute solution appears to exist mainly as $\dot{H}$ $HCrO_4'$ and CrO_4'' ions and dichromates as $HCrO_4'$ and CrO_4'' ions.

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Changes in the Viscosity of Gelatine Sols in the process of Gelation.

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It has been observed that the melting and setting temperatures of gelatine gels and sols are not identical. The difference observed in the melting and setting temperatures of gelatine gels and sols becomes smaller with increasing time of observation. Moreover, melting point determinations of gels, as recorded by different workers, are not reproducible. Our researches show that the setting and melting temperatures are identical, if sufficient time be allowed for observation.

In the course of our observations on the hysteresis in the sol-gel transformation of gelatine gels of various concentrations the following results were obtained, for different intervals of time.

Table I.

Conc. (%).		10			20				40		
Melting	Temp.	35°	30°	25°	40°	35°	30°		40°	35°	30°
	Time (min.)	2	4	*	2	3	*		3	9	*
Solidifying	Temp.	20°	25°	30°	20°	25°	30°	35°	25°	30°	35°
	Time (min.)	6	17	**	3	5	14	**	2	7	**

* Does not melt in 1 hr. ** Does not set in 1 hr.

By extrapolating our results, we find that the melting and setting points become identical for 10 per cent. gelatine sol in 35 minutes, for 20 per cent. gelatine sol in 25 minutes and for 40 per cent. gelatine sol in 20 minutes. That is, the greater the concentration of the gel, the less is the time at which the melting and setting temperatures become the same. Similar results were obtained with soap gels in various alcohols and water. It will also be found from the above table, that no firm gels of gelatine of any concentration can be obtained above 33°.

It is well known that the gelatine sols show remarkable change in viscosity on keeping. P. von Schroeder (*Z. physikal. Chem.*, 1903, **43**, 75) recognised that when a gelatine solution is kept at a high temperature, at which it does not gelatinise, the viscosity decreases continuously until it reaches a considerably low value. On the other hand, he showed that when a gelatine solution is kept at its setting temperature or below it, the viscosity regularly increases till it finally sets. Arisz (*Koll. Chem. Beih.*, 1915, **7**, 1) has also shown with an Ostwald-viscometer for glycero sols of gelatine that the viscosity of a gelatine sol, at its temperature of setting, is always less than the viscosity of the same gelatine sol when obtained from the gel condition. If, however, the gelatine sols be kept at the temperature of observation for a preferably long time, the viscosities approach the same value. Similarly it has been reported by Davies and co-workers (*J. Amer. Chem. Soc.*, 1921, **43**, 1526) that the viscosity of gelatine solutions increases with the age. We have noticed remarkable changes in viscosity of gelatine sols with ageing, at temperatures not far off from their melting and setting temperatures, and hence a measurement of viscosity near the melting or the setting temperatures is important. We have already reported that in all the sol-gel transformations, the phenomenon of hysteresis is remarkably diminished by sowing the sols, which are in the process of gelation, with the already formed gels of the same substance. We have, therefore, also investigated the effect of sowing of gels on the viscosity of gelatine sols.

In our investigations, we have used Kahlbaum's Goldrück sample and the following results were obtained on the moisture, ash content and p_H of the solution.

Moisture—10·28 per cent.; Ash—1·24 per cent.
p_H (colorimetric, Michaelis' method)—5·3.

Gelatine sols of various concentrations were prepared as far as possible under identical conditions. Each sol was divided into two parts, I and II. Part I was immediately brought to the temperature of the thermostat, maintained at 45° ±0·5° and then the temperature of the thermostat was lowered by 5° up to 25° for the observation of the viscosities at the lower temperatures. Part II was first allowed to set and kept in the thermostat at 25° and then the temperature was gradually increased by 5° up to 45° for the observation of viscosities at the higher temperatures.

TABLE II.

Gelatine sol (2%).

Temp.	Time (min.)		45°	40°	35°	30°	25°
Abs. viscosity (Parts I & II).	6	I	0·01088	0·01126	0·01237	0·01332	0·01752
		II	0·01065	0·01127	0·01244	0·01402	0·01790
	11	I	0·01088	0·01129	0·01233	0·01339	0·01762
		II	0·01062	0·01115	0·01226	0·01384	0·01781
	16	I	0·01088	0·01129	0·01239	0·01339	0·01780
		II	0·01062	0·01112	0·01218	0·01376	0·01781

The viscosities were measured by Ostwald's viscometer. The changes in the viscosity with time and temperature in the two cases are given below.

TABLE III.

Gelatine sol (3 %).

Temp.	Time (min.)	Absolute viscosity.	
		Part I	Part II
45°	6·5	0·01403	0·01439
	11·5	0·01407	0·01439
	16·5	0·01415	0·01430
40°	6·5	0·01638	0·01632
	11·5	0·01653	0·01616
	16·5	0·01665	0·01616
35°	7	0·01883	0·01963
	12	0·01884	0·01868
30°	7	0·01895	0·01851
	8	0·02191	0·02647
	15	0·02227	0·02554
	21	0·02254	0·02509
25°	15	0·03218	0·04444
	22	0·04291	0·03026

TABLE IV$_8$

Gelatine sol (10%).

Temp.	Time (min.)	Absolute viscosity.	
		Part I	Part II
50°	12	0·06553	0·06170
	32	0·06770	0·06060
45°	12	0·07426	0·06760
	33	0·07585	0·06633
40°	25	0·9303	0·07326
35°	—	Extremely viscous.	Extremely viscous.
30°	—	,,	,,
25°	—	Sets to a jelly.	Jelly.

It is observed that there is a considerable difference in the viscosities of the gelatine sols prepared at a higher and a lower temperature (also *cf.* Davies and co-workers, *loc. cit.*), the sol prepared at a lower temperature showing greater viscosity than the sol prepared at a lower temperature. Our results show that in general the viscosity increases with time when a gelatine sol prepared at a higher temperature is kept in a bath of a lower temperature, whilst the sol obtained from a gel shows a decrease in the viscosity with time, at a temperature higher than the melting point of the gel.

It will be apparent from our results that in the case of 2% gelatine sols, the ageing effect on the viscosity (a decrease or increase) is appreciable even within a short interval of time from a temperature of about 35°; in the case of 3% sol, this change appears from 40° and in the case of 10% sol, this is observable even at 50°. It is therefore evident that the change in the viscosities of gelatine solutions with time may be either towards an increase or decrease, according to the condition of the solution under investigation. The changes with time are also maximum at the temperature nearing gelation or melting points in the sol-gel transformation and the effect of time continuously diminishes, as the temperature is increased and is far beyond the melting or setting temperature.

Davies and Oakes (*loc. cit.*) observed that the viscosity of a sample of 1% gelatine solution, when kept in a bath of 35° immediately after its preparation, showed a tendency of increase. The

sample, previously set to a firm gel and kept at 30°, also showed a similar change. As the viscosity measurements were carried out by them, in viscometer tubes, it is apparent that the gel must have melted to a less viscous mobile liquid, which again showed an increase in viscosity. This latter result appears to us rather peculiar and accordingly, we have carried out a similar set of experiments with gelatine sols.

In the following cases, the viscosities were determined under two conditions, namely, the sol was (*i*) brought down from 50° to the lower temperature at which the viscosities were determined and (*ii*) allowed first to set, then kept in the ice chest for one hour and again brought to the temperature of observation.

The setting temperatures of a 3% sol of p_H 7·6 and a 10% sol of p_H 7·7 were 15° and 23° respectively.

TABLE V.

Gelatine sol (3%); $p_H = 7{\cdot}6$.

Case 1.					Case 2.				
Temp. = 35°					Temp. = 35°				
Time (min.)	10	85	123	145	Time (min.)	60	120	200	275
Viscosity	0·02276	0·02304	0·2332	0·02345	Viscosity	0·02376	0·02334	0·02325	0·02313
Temp. = 45°					Temp. = 45°				
Time (min.)	15	48	85	125	Time (min.)	60	120	180	240
Viscosity	0·0174	0·01756	0·01763	0·01776	Viscosity	0·01568	0·01558	0·01550	0·01545

TABLE VI.

Gelatine sol (10%); $p_H = 7{\cdot}7$.

Case 1.				Case 2.				
Temp. = 35°				Temp. = 35°				
Time (min.)	15	68	130	Time (min.)	75	140	200	250
Viscosity	0·1043	0·1077	0·1127	Viscosity	0·1048	0·1033	0·1020	0·1017
Temp. = 45°				Temp. = 45°				
Time (min.)	20	68	127	190	Time (min.)	60	130	200	250
Viscosity	0·08813	0·08854	0·08880	0·08896	Viscosity	0·08842	0·08450	0·07758	0·07142

It thus appears that 3 per cent. and 10 per cent. gelatine sols show an increase in viscosity with ageing, when brought down to 45°

or 35° from a higher temperature. On the other hand, the viscosity decreases when the sols are kept at 35° or 45° after they have formed gels, and hence our results are not in agreement with those of Davies and co-workers.

In a series of publications (*Z. anorg. Chem.*, 1929, **184**, 135; *J. Indian Chem. Soc.*, 1929, **6**, 17) from these laboratories, we have shown that the sols of silicic, vanadic, tungstic, molybdic and antimonic acids contain sufficient quantities of these substances in the molecular condition, simple and aggregated, together with the colloidal particles. The simple molecules have a general tendency to aggregate and gradually merge into particles of colloidal dimension with age. Raising the temperature of the sol, when freshly prepared, causes the disintegration of the colloidal particles and aggregated molecules into simpler ones. Similar transition of the particles of the bigger size to the smaller size has been followed with gelatine sol during the process of heating. Arisz (*Koll. Chem. Beih.*, 1915, **7**, 22) showed that the Tyndall cone is very faint in gelatine sols at 70°, it gradually becomes stronger on cooling and weaker on rewarming. He found that the variations in the viscosity of gelatine sols were parallel with the changes in the strength of the Tyndall cone. Bachmann (*Z. anorg. Chem.*, 1911, **73**, 125; 1912, **79**, 202) has also found similar behaviour from ultramicroscopic observations during the gelation of silicic acid, gelatine and agar. It is therefore to be concluded that gelatine solutions at higher temperatures contain extremely fine particles of molecular dimensions which gradually polymerise to bigger aggregates and colloidal particles on cooling the sols.

We are of the opinion that in the gelatine solution, the following equilibrium exists:—

Gelatine simple molecules $\rightleftharpoons$ Gelatine aggregated molecules $\rightleftharpoons$ Colloidal gelatine.

Smith (*J. Amer. Chem. Soc.*, 1919, **41**, 135) from his observations on the mutarotation of gelatine at various temperatures concludes: "At any intermediate temperature between 35° and 15°, there is a condition of equilibrium which may be represented by the equation

$$\text{Sol form A} \rightleftharpoons \text{Gel form B}$$

He believes that an increase in the form B parallels an increase in the viscosity.

Smith (*loc. cit.*) believes that a transition of the sol form A to gel form B is due to a polymerisation of gelatine molecules. Moore and Roaf (*Biochem. J.*, 1907, **2**, 52) have shown from osmotic pressure measurements, that there is an aggregation of molecules, responsible for the change of osmotic pressure with time. Bogue (*J. Amer. Chem. Soc.*, 1922, **44**, 1913) has shown that the rate of flow of gelatine sols in viscosity tube, plotted against the shearing stress, gives a straight line, which passes through the origin at higher temperatures. If, however, the temperature of gelatine sol be gradually lowered, the increase in the viscosity is rapid with the fall of the temperature, near the gelation point, and with the varying shearing stress, the rate of fall is hardly linear, especially with the lower values of the stress. It is found that the curves, when extrapolated, do not pass through the origin. From these results, it is apparent that the gelatine sol shows a plastic flow near the gelation temperature, indicating the formation of large number of colloidal particles at the expense of aggregated and simple molecules, present in the sol.

We are of opinion that in gelations, as observed in the reversible sol-gel transformations, an aggregation of simple molecules is an inevitable consequence. Thus in the case of gelatine sols, gelation occurs when a sufficient quantity of aggregated molecules and colloidal particles are present. As the number of aggregated molecules and necessarily the colloidal particles is smaller in a dilute solution than in a concentrated one, it is evident that a greater lowering of temperature is necessary for the formation of the gel from a dilute solution than from a concentrated one. As however the amount of aggregated molecules rapidly diminishes with increasing temperature, it follows that gelation cannot take place above a certain temperature, with any concentration of gelatine sols. Thus with gelatine sols of various concentrations, no gel is obtained even with 40 per cent. solution above 33°. Our viscosity measurements on 10 per cent. gelatine sol show a distinct change with time even at a temperature of 50° and we are of opinion that an increase in viscosity with time is associated with the formation of more and more of aggregated molecules and *vice versa*.

It may be of interest to add here that Andrade in a recent communication (*Nature*, 1930, **125**, 583) also remarks: "True association, in which the molecules are bound together in clusters of two or more for a time large compared to the intervals between collisons, leads, with the mechanism postulated, to an increase of viscosity." A

sudden increase, in the viscosity of gelatine sols with the fall in temperature near the setting temperature is most probably due to the formation of a large number of aggregated molecules and colliodal gelatine, near the gelation temperature.

It may be stated here that sol form A and gel form B of Smith correspond to simple and aggregated molecules. Above 35°, the number of simple molecules preponderates and at 16°, there is an abundance of aggregated molecules and colloidal gelatine. Between 16° and 35°, the transformation of simple molecules to aggregated molecules and colloidal gelatine is very rapid, with the lowering of temperature. Davies and Oakes (*loc. cit.*) have concluded from the ageing effect on the viscosity of gelatine sols that the existence of the gel form B is only possible below 38°, as the viscosity of gelatine sols continuously increases with age below this temperature and above this, the viscosity decreases with age. Our experimental results with the gelatine sols of a high concentration (10%) however distinctly show an increase in the viscosity with age, when prepared at a higher temperature and then kept for observation even at 50°. On the other hand, with dilute gelatine sols (2 and 3%), changes in viscosity with ageing were only significant between temperatures 35° and 40° and below.

In the previous publication (*loc.cit.*) from this laboratory, we have shown that sowing the reversible sols with already formed gels more readily affects the gelation of sols. The results recorded in the following table show a remarkable increase in the viscosity of the sol, when it is sowed with already formed gel of the same concentration as the sol.

Table VII.

Viscosity changes with Sowing.

gelatine sol (2%).

Without sowing.				*With sowing.*			
Temp.	Time (min.).	30°	35°	Temp.	Time (min.).	30°	35°
Viscosity	12	0·01850	0·01448	Viscosity	13	0·02305	0·02186
	22	0·01875	0·01448		23	0·02319	0·02186
	32	0·01906	0·01448		33	0·02333	0·02186

It is interesting to find that there is a greater percentage of increase in the viscosity of the sol, kept at a higher temperature (35°) than at a lower temperature (30°). An increase in the viscosity of sols of gelatine in the presence of already formed, gels show that more of aggregated molecules and colloidal gelatine are formed when the gels are added to the sols. As the sols at 30° contain greater number of aggregated molecules and colloidal gelatine than at 35°, it is apparent that the effect of sowing is more marked at 35° than at 30°. It must be understood that at temperatures above 35°, this effect of sowing, namely to cause an increase in viscosity, will decrease, because the gel melts quickly at temperatures above 35° and thus the aggregating influence on the molecules present in the gelatine sols becomes less effective.

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Mono-substituted Carbohydrazides, their Typical Derivatives and Formation of Heterocyclic Compounds from them.

By Praphulla Chandra Guha and Md. Abdul Hye.

Although carbohydrazide and its *sym.*-diphenyl-derivative have been prepared by Curtius and Reich (*J. pr. Chem.*, 1895, *ii*, **52**, 469), Skinner and Ruheman (*J. Chem. Soc.*, 1888, **53**, 550). Cazeneuve and Moreau (*Compt. rend.*, 1899, **129**, 1256), Fischer and Heller, (*Annalen*, 1891, **263**, 277, 269), Fischer (*Ber.*, 1889, **22**, 1935) and Pellizary (*Gazzetta*, 1886, **16**, 200), monosubstituted carbohydrazides are not known. The present investigation was undertaken with a view to make a comparative study of monosubstituted carbohydrazides and their derivatives with those of monosubstituted thiocarbohydrazides (Guha and Roy-Chaudhury, *J. Indian Chem. Soc.*, 1928, **5**, 149, 163).

Phenyl-, *o*-tolyl- and *p*-tolyl-carbohydrazides have now been prepared by the action of hydrazine hydrate upon the corresponding ethyl carbazinates, thus:

$$RNH{\cdot}NH{\cdot}CO_2Et + H_2N-NH_2 \longrightarrow RNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$$

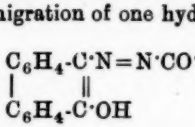
(R = Ph, *o*-tolyl, and *p*-tolyl)

But the reaction between phenylhydrazine and ethyl phenylcarbazinate did not take place.

Phenyl-, *o*- and *p*-tolyl-carbohydrazides react with aldehydes to give carbohydrazones of the type, $RNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N:CHR'$ (R = Ph, R′ = Ph, cinnamyl, *o*-chlorophenyl, *p*-chlorophenyl, *m*-bromophenyl, *o*-nitro-phenyl, *m*-nitrophenyl, *o*-hydroxyphenyl; R = *o*-tolyl, R′ = Ph, *o*- and *p*-chlrophenyl, *o*- and *p*-nitrophenyl, *m*-bromophenyl, *o*-hydroxyphenyl; R = *p*-tolyl, R′ = Ph). *m*-Phthalaldehyde and 1-phenyl- and 1-*p*-tolyl-carbohydrazide gave respectively $m\text{-}C_6H_4(CH:N{\cdot}NH{\cdot}CO{\cdot}N{\cdot}H{\cdot}NHPh)_2$ and $m\text{-}C_6H_4(CH=N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3)_2$ while acetone yielded the expected compounds, $Ph{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N:CMe_2$ and $Me{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N:CMe_2$.

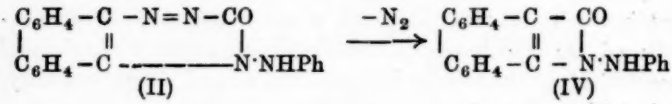
The oxidising and ring-closing action of ferric chloride upon 1-phenylcarbohydrazide was tried by analogy with a similar reaction of Guha and Roy-Chaudhury with the corresponding thio-compound where they obtained a thiodiazol (*loc. cit.*, p. 157). But, in the present instance, the reaction could not be made to take place even when the reactants were heated in a sealed tube.

Phenanthraquinone and phenylcarbohydrazide yield first of all the monophenylcarbohydrazone, which then assumes the azo-structure (I) by the migration of one hydrogen atom.

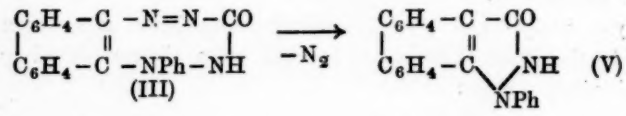


(I)

This loses a molecule of water forming a closed-ring compound (possibly II or III) which, being unstable, is converted into the compound (IV or V) by loss of nitrogen. The former structure is preferred as the compound is insoluble in alkali.



(II) (IV)



(III) (V)

Similar reactions involving the elimination of nitrogen from heterocyclic compounds have recently been observed by De and Dutt (*private communication*) with compounds obtained from phenanthraquinone on the one hand and 4-substituted thiosemicarbazides, diarylaminoguanidines, etc., on the other.

Isatin yields the corresponding phenyl- or *o*-tolylcarbohydrazone. From isatin and phenylthiocarbohydrazide Guha and Roy-Choudhury (*loc. cit.*, p. 152) obtained a thiodiazine compound. Evidently, the sulphur atom of the thiocarbohydrazones can assume the thiol form readily, but the oxygen atom of the carbohydrazones cannot assume the hydroxylic form so easily.

Carbon bisulphide in presence of alcoholic potash reacts with the hydrazide at the ordinary temperature to yield the expected potassium dithiocarboxylate (VI). If, however, the reaction mixture

is boiled under reflux for several hours, the potassium salt yields 1-*N*-phenylmonothiourazine (VII), thus:

$$\underset{\text{(VI)}}{PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CS_2K} \xrightarrow{-KSH} HS{\cdot}C\begin{matrix} N - NH \\ \diagdown\!\!\diagup \\ NPh - NH \end{matrix}\!\!>CO \quad \underset{\text{(VII)}}{}$$

It will be seen that this reaction is quite similar to that observed by Guha and De (*J. Chem. Soc.*, 1924, **125**, 1216) between carbon bisulphide aud thiocarbohydrazide.

Chlorocarbonic ester reacts very readily to form carbethoxyphenylcarbohydrazide (VIII) which, on being treated with strong hydrochloric acid, is decomposed, thus:

$$\underset{\text{(VIII)}}{Ph{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO_2Et} + H_2O = Ph{\cdot}NH{\cdot}NH_2 + NH_2.NH_2 + 2CO_2 + C_2H_5OH.$$

The influence of the phenyl group of phenylcarbohydrazide in not allowing the reactions to proceed in the normal way (as in the case of the unsubstituted carbohydrazide) is well marked also in its behaviour towards carbamide. Instead of forming a *p*-urazine derivative (*vide* Guha and De, *loc. cit.*) it forms phenylcarbohydrazidecarbonamide (IX), thus:

$$Ph{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2 + NH_2CO{\cdot}NH_2 \rightarrow \underset{\text{(IX)}}{Ph{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2} + NH_3$$

Nitrous acid reacts with the hydrazide in a peculiar fashion yielding not the expected azoimide ($PhNH{\cdot}NH{\cdot}CO{\cdot}N_3$) but 1-phenyl-4-hydroxysemicarbazide (X) by the elimination of a molecule of nitrogen from the intermediate azo-compound, thus:

$$PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2 \xrightarrow{NHO_2} PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N{:}N{\cdot}OH$$

$$\xrightarrow{-N_2} \underset{\text{(X)}}{PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}OH}$$

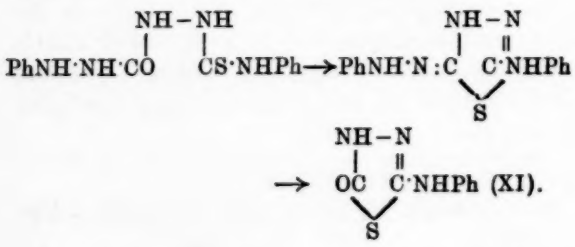
It might be mentioned in this connection that this is the first time that a 4-hydroxysemicarbazide has been prepared.

Phenyl*iso*cyanate and potassium cyanate react with phenylcarbohydrazide in the normal fashion to yield phenylcarbohydrazidecarbophenylamide, $PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NHPh$ and phenylcarbohydrazidecarbonamide $PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, the latter

being identical with the compound obtained by the action of urea. Ring closure of these compounds could not be effected even by boiling with strong hydrochloric acid for six hours. The corresponding phenyl*iso*cyanate derivative of phenylthiocarbohydrazide readily gives a triazine by the action of potassium hydroxide, hydrochloric acid, etc. (*cf.* Guha and Roy-Choudhury, *loc. cit.*).

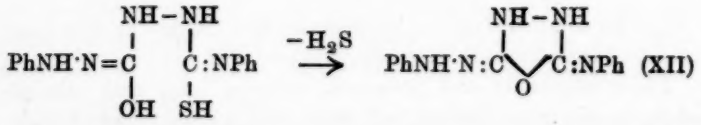
Phenyl- and *o*-tolylcarbohydrazides react readily with thiocarbimides to form the corresponding carbothioarylamides, RNH·NH·CO·NH·NH·CS·NHR′ (R=Ph, R′=Ph, *o*-totyl, *p*-tolyl, xylyl, allyl, ethyl ; R=*o*-tolyl, R′=Ph, *o*-tolyl, *p*-tolyl, xylyl, allyl, β-naphthyl).

The ring-closure of this type of compounds has been effected with strong hydrochloric acid, potassium hydroxide or ferric chloride. Phenylcarbohydrazidecarbothiophenylamide, on being treated with strong hydrochloric acid or ferric chloride gives 2-keto-5-phenylamino-2:3-dihydro-1:3:4-thiodiazole (XI).



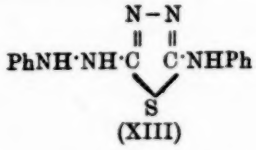
The substance is insoluble in dilute acid and alkali and is identical with the compound prepared by Guha and Sen (*J. Indian Chem. Soc.*, 1927, **4**, 43) by the action of urea on 4-phenylthiosemicarbazide.

Phenylcarbohydrazidecarbothiophenylamide on being treated with 20% potassium hydroxide yields 2-phenylhydrazino-5-phenylimino-2:3:4:5-tetrahydro-1:3:4-oxdiazole (XII) by the loss of one molecule of hydrogen sulphide, thus:

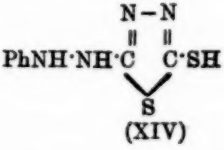


The behaviour of phenylthiocarbohydrazidecarbothiophenylamide towards hydrochloric acid and alkali (*cf.* Guha and Roy-Choudhury,

loc. cit.) does not very much resemble that of phenylcarbohydrazidecarbothiophenylamide in so far as the latter gives, on alkali treatment, two thiodiazole compounds (XIII and XIV),



(XIII)



(XIV)

and with hydrochloric acid, 2:5-diketotetrahydro-1:3:4-thiodiazole. Thiodiazoles of the type of (XI) have been prepared by Busch (*Ber.*, 1901, **34**, 320, 2328 ; 1902, **35**, 973 ; 1904, **37**, 2333 ; 1909, **42**, 4763 ; 1911, **44**, 561, 1580) and by Freund (*Ber.*, 1891, **24**, 4178) by the action of carbonyl chloride upon 1:4-diarylthiosemicarbazides, and by Guha and Sen (*loc. cit.*) by the action of urea upon 4-arylthiosemicarbazides.

Experimental.

1-*Phenylcarbohydrazide.*—About 30 experiments were performed to find out the best method of preparation of 1-phenylcarbohydrazide from phenylcarbazinic ester and hydrazine hydrate in alcoholic solution under varying conditions of temperature (*viz.*, from 100° to 150° under reflux and in a sealed tube) and duration of heating (*viz.*, from 5 to 15 hours) as the result of which the method given below has been found to be the best.

A mixture of ethyl phenylcarbazinate (10 g.) and hydrazine hydrate (3·5 g.) with 4 c.c. of absolute alcohol was heated in a sealed tube at 120-125° for 12 hours. A slight pressure was noticed inside the tube after the reaction. The solution was poured into water and the unaltered ester (4 g.) was filtered off. The filtrate was evaporated on a water-bath to a syrup which on being kept in a vacuum desiccator for 2 days formed a white crystalline mass. This was washed with ether to remove some tarry matters and was finally crystallised from alcohol (yield, 5·5 g.). It is readily soluble in water, alcohol and acetic acid and sparingly so in benzene, toluene and ether. (Found: N, 33·78. $C_7H_{10}ON_4$ requires N, 33·93 per cent.). When the temperature was kept low (say between 100° and 120°) most of the carbazinic ester was recovered unchanged—whilst on the application of higher temperature (130°-150°) a brownish-yellow tarry product was obtained from which a small quantity of carbohydrazide

melting at 154° was isolated. (Found: N, 62·15. Calc., N, 62·22 per cent.).

Attempt to prepare sym-*Diphenylcarbohydrazide*.—A mixture of equivalent quantities of ethyl phenylcarbazinate and phenylhydrazine was heated in a sealed tube at 120°—125° and again at 140-150° when no reaction was found to have taken place.

Reaction with o-*Phenylenediamine*.—Ethyl phenylcarbazinate (10 g.) was thoroughly mixed with an equivalent quantity of *o*-phenylenediamine and heated on an oil-bath at 200-210° for several hours but no reaction was found to have taken place. Guha and Roy-Choudhury (*J. Indian Chem. Soc.*, 1928, **5**, 168) prepared a benzothioltriazine by the action of *o*-phenylenediamine upon ethyl phenyldithiocarbazinate.

Ethyl o-*Tolylcarbazinate*.—To a mixture of *o*-tolylhydrazine and pyridine, 4 to 5 times the quantity of water was added and the solution cooled to 0°. To this solution one molecular proportion of ethyl chlorocarbonate was added drop by drop under brisk shaking when an oil separated which soon solidified. The crude product was washed with dilute acetic acid and was further purified by crystallisation from alcohol, m.p. 74—75° (yield quantitative).

1-o-*Tolylcarbohydrazide*.—A mixture of equivalent quantities of ethyl *o*-tolylcarbazinate (10 g.), hydrazine hydrate (4 g.) and absolute alcohol (4 c.c.) was heated in a sealed tube at 115-120° for 12 hours. The solution was then poured into water, when the unreacted ester (about 3 g.) precipitated out and the whole mass was thoroughly triturated in a mortar and filtered. The filtrate was evaporated to dryness on a water-bath and the solid thus obtained crystallised from alcohol, m.p. 153° (yield, 4 g.). It is readily soluble in water, alcohol and acetic acid. (Found: N, 30·89. $C_8H_{12}ON_4$ requires N, 31·11 per cent.).

Ethyl p-*Tolylcarbazinate*.—It was prepared similarly as the phenyl derivative and crystallised from a large quantity of water; m.p. 89-90° (yield quantitative).

1-p-*Tolylcarbohydrazide*.—The method of preparation was the same as that of 1-*o*-tolylcarbohydrazide. It was crystallised from water; m.p. 148-149° (yield almost quantitative). It is readily soluble in water, alcohol and acetic acid. (Found: N, 31·56. $C_8H_{12}ON_4$ requires N, 31·11 per cent.)

Benzaldehyde-1-*phenylcarbohydrazone*.—Benzaldehyde (1 g.) and 1-phenylcarbohydrazide (1·6 g.) in alcoholic solution were heated

under reflux for a few minutes, when a white crystalline product separated out.

It was filtered, washed with alcohol and then crystallised from the same solvent, m. p. 210-211° (yield quantitative). (Found: N, 22·52. $C_{14}H_{14}ON_4$ requires N, 22·04 per cent.).

o-*Chlorobenzaldehyde*-1-o-*tolylcarbohydrazone* was similarly prepared and crystallised from acetic acid ; m.p. 212-213°. (Found: N, 18·74. $C_{15}H_{15}OClN_4$ repuires N, 18·51 per cent.).

o-*Chlorobenzaldehyde*-1-*phenylcarbohydrazone* was crystallised from acetic acid, m.p. 212-213°.

p-*Chlorobenzaldehyde*-1-*phenylcarbohydrazone* was crystallised from acetic acid, m.p. 197-198°.

m-*Bromobenzaldehyde*-1-*phenylcarbohydrazone* was crystallised from acetic acid, m.p. 196-197°.

o-*Nitrobenzaldehyde*-1-*phenylcarbohydrazone* was crystallised from alcohol, m.p. 208-209°.

m-*Nitrobenzaldehyde*-1-*phenylcarbohydrazone*, m.p. 243-244°.

Salicylaldehyde-1-*phenylcarbohydrazone* was crystallised from acetic acid, m.p. 222-23°. It is soluble in alkali and can be precipitated by acids.

Benzaldehyde-1-o-*tolylcarbohydrazone*, m.p. 201-202°, was crystallised from alcohol.

o-*Chlorobenzaldehyde*-1-o-*tolylcarbohydrazone*, m.p. 212-213°, was crystallised from acetic acid.

p-*Chlorobenzaldehyde*-1-o-*tolylcarbohydrazone*, m.p. 198°, was crystallised from acetic acid.

o-*Nitrobenzaldehyde*-1-o-*tolylcarbohydrazone*, m. p. 219°, was crystallised from acetic acid.

m-*Nitrobenzaldehyde*-1-o-*tolylcarbohydazone*, m.p. 211-212°, was crystallised from acetic acid.

m-*Bromobenzaldehyde*-1-o-*tolylcarbohydrazone*, m.p. 216°, was crystallised from acetic acid, m.p. 216°. (Found: N, 16·27. $C_{15}H_{15}OBrN_4$ requires N, 16·13 per cent.).

Salicylaldehyde-1-o-*tolylcarbohydrazone* was crystallised from acetic acid, m.p. 218-219°. It is soluble in alkali and can be precipitated by acids. (Found: N, 19·68. $C_{15}H_{16}O_2N_4$ requires N, 19·71 per cent.).

Benzaldehyde-1-p-*tolylcarbohydrazone* was crystallised from alcohol, m.p. 193-194°. (Found: N, 21·20. $C_{15}H_{16}ON_4$ requires N, 20·89 per cent.).

m-*Phthalaldehyde*-1-*phenylcarbohydrazone*, m.p. 266-267°. It is insoluble in almost all organic solvents and was purified by washing with boiling alcohol repeatedly.

m-*Phthalaldehyde*-1-o-*tolylcarbohydrazone* was prepared similarly. It was insoluble in almost all the organic solvents but slightly soluble in alcohol from which it was precipitated in an amorphous state, m.p. 236-237° (decomp.). (Found: N, 24·49. $C_{24}H_{26}O_2N_8$ requires N, 24·46 per cent.).

Acetone-1-*phenylcarbohydrazone*, m.p. 83°. (Found: N, 27·04. $C_{10}H_{10}ON_4$ requires N, 27·18 per cent.).

Acetone-1-o-*tolylcarbohydrazone*, m.p. 177°, was crystallised from acetone.

Action of Phenanthraquinone on 1-*Phenylcarbohydrazide* (IV).—Phenanthraquinone and 1-phenylcarbohydrazide (in equivalent quantities) were heated under reflux for 5-6 hours in acetic acid solution when nitrogen was found to evolve. The separated solid crystallised from nitrobenzene; m.p. 285° (decomp.). It is insoluble in acids and alkalis and is charred by concentrated sulphuric acid. (Found: N, 9·52. $C_{21}H_{14}ON_2$ requires N, 9·03 per cent.).

Isatin-1-*phenylcarbohydrazone*.—A mixture of 1-phenylcarbohydrazide and isatin in acetic acid was heated under reflux for about 4 hours. Within an hour the colour of the solution changed from red to yellow and a yellow precipitate came out of the solution. It was filtered, washed with acetic acid and crystallised from pyridine; m.p. 281° (decomp.). It is soluble in alkali and can be precipitated back by acids. (Found: N, 23·62. $C_{15}H_{13}O_2N_5$ requires N, 23·73 per cent.).

Isatin-o-*tolylcarbohydrazone*.—Molecular proportions of 1-o-tolylcarbohydrazide (1 g.) and isatin (0·81 g.) were heated in acetic acid solution for 2 hours. The separated yellow product crystallised from acetic acid in needles, m.p. 251—252° (decomp.). It is readily soluble in alkali from which solution it can be precipitated by acids. (Found: N, 23·38. $C_{16}H_{15}O_2N_5$ requires N, 22·65 per cent.).

Potassium 1-*Phenylcarbohydrazide-dithiocarboxylate*, $PhNH{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CS_2K$ (VI).—A molecular quantities of 1-phenylcarbohydrazide, carbon bisulphide and caustic potash in absolute alcohol on being allowed to stand for some time gave a white crystalline

substance which was further purified by crystallising from the same solvent. (Found : N, 20·02. $C_8H_9ON_4S_2K$ requires N, 19·93 per cent.).

1-Phenyl-6-thiol-3-keto-1 : 2 : 3 : 4-tetrahydro-1 : 2 : 4 : 5-tetrazine (VII).—A mixture of equivalent quantities of 1-phenylcarbohydrazide, carbon bisulphide and caustic potash in absolute alcohol was heated under reflux at 60-70° for about 2 hours and subsequently on a water-bath for 4 hours. The pasty mass obtained after the removal of alcohol was dissolved in water, filtered and cautiously acidified with hydrochloric acid. On cooling, a white crystalline precipitate came out of the solution slowly and was crystallised from acetic acid, m.p. 206°. (Found: C, 46·51; H, 4·42 ; N, 27·06, 26·86. $C_8H_8ON_4S$ requires C, 46·15 ; H, 3·85 ; N, 27·32 per cent.).

5-Carbethoxy-1-phenylcarbohydrazide (VIII).—To a well cooled aqueous solution of 1-phenylcarbohydrazide an equivalent quantity of ethyl chlorocarbonate was added drop by drop. The white crystalline substance thus obtained was filtered, washed with water and crystallised from alcohol, m.p. 202-203°. (Found: N, 23·94. $C_{10}H_{14}O_3N_4$ requires N, 23·52 per cent.).

Urea and 1-Phenylcarbohydrazide: Formation of 1-Phenylcarbohydrazide-5-carbonamide (IX).—An intimate mixture of molecular proportions of freshly dried urea and 1-phenylcarbohydrazide was heated on an oil-bath at 130-135° for 6-7 hours. First of all the mixture melted and the reaction proceeded with the evolution of ammonia. After about two hours the molten mass solidified, but as the evolution of ammonia still continued it was heated for 5 hours more. The solid was then crystallised thrice from water ; m.p. 223° (decomp.). (Found: N, 33·56. $C_8H_{11}O_2N_5$ requires N, 33·49 per cent.)

Action of Nitrous Acid upon 1-Phenylcarbohydrazide: Formation of $PhNH{\cdot}NH{\cdot}CO{\cdot}NHOH$ (X).—To a mixture of ice-cold aqueous solution of 1-phenylcarbohydrazide (1 mol.), and sodium nitrite (1 mol.), ice-cold hydrochloric acid (2 mols.) was added drop by drop when nitrogen was found to evolve profusely. The separated yellow pasty mass which solidified on standing, was freed from the adhering oily impurity by pressing on a porous plate and was finally crystallised from 88 per cent. alcohol; m.p. 86°. It is insoluble in cold acid but dissolves in alkali on being gently warmed with a dull yellow coloration. (Found: C, 50·25; H, 5·58; N, 27·00, 26·81, 26·54. $C_7H_9O_2N_3$ requires C, 50·36 ; H, 5·40 ; N, 27·00 per cent.).

Action of Potassium Cyanate: *Formation of* (IX).—To an aqueous solution of the carbohydrazide an equivalent quantity of hydrochloric acid was added. The solution was then cooled and an equivalent quantity of an aqueous solution of potassium cyanate gradually added under shaking. The white precipitate thus obtained was crystallised from water ; m.p. 223°. It is identical with compound (IX) as obtained by the action of urea. (Found: N, 33·56. $C_8H_{11}O_2N_5$ requires N, 33·49 per cent.)

1-*Phenylcarbohydrazide-5-carbophenylamide*, PhNH·NH·CO·NH ·NH·CO·NHPh.—To a well cooled aqueous solution of 1-phenylcarbohydrazide (1 mol.), phenyl*iso*cyanate (1 mol.) was added drop by drop under shaking. A white precipitate was obtained almost instantaneously which was filtered, washed with water and crystallised from alcohol; m.p. 218-219°. (Found: N, 24·79. $C_{14}H_{15}O_2N_5$ requires N, 24·56 per cent.). When boiled with strong hydrochloric acid it was left quite unchanged.

1-*Phenylcarbohydrazide-5-thiocarbophenylamide*, PhNH·NH·CO ·NH·NH·CS·NHPh.—An alcoholic solution of a mixture of molecular quantities of 1-phenylcarbohydrazide and phenyl mustard oil was heated under reflux for 15 minutes. A white precipitate was obtained which was filtered and washed with alcohol. It is almost insoluble in alcohol, acetic acid, and other organic solvents, except pyridine from which it is crystallised ; m.p. 196° (decomp.) (yield quantitative). (Found: N, 23·10. $C_{14}H_{15}ON_5S$ requires N, 23·25 per cent.). The following compounds were prepared similarly and crystallised from large quantities of alcohol. They are all soluble in alkali and can be precipitated back by hydrochloric acid.

1-*Phenylcarbohydrazide-5-thiocarbo-o-tolylamide*, m.p. 175—176°. (Found: N, 22·28. $C_{15}H_{17}ON_5S$ requires N, 22·22 per cent.).

1-*Phenylcarbohydrazide-5-thiocarbo-p-tolylamide*, m.p. 196—197° (decomp.). (Found: N, 22·30. $C_{15}H_{17}ON_5S$ requires N, 22·22 per cent.).

1-*Phenylcarbohydrazide-5-thiocarbo*-1:3:4-*xylylamide*, m.p. 179—180°. (Found: N, 21·40. $C_{16}H_{19}ON_5S$ requires N, 21·27 per cent.).

1-*Phenylcarbohydrazide - 5 - thiocarboallylamide*, m. p. 196°. (Found: N, 26·47. $C_{11}H_{15}ON_5S$ requires N, 26·41 per cent.).

1 - *Phenylcarbohydrazide - 5 - thiocarbomethylamide*, m.p. 207°. (Found: N, 27·74. $C_{10}H_{15}ON_5S$ requires N, 27·66 per cent.).

1-o-*Tolylcarbohydrazide-5-thiocarbophenylamide*, m.p. 194—195° (decomp.). (Found: N, 22·37. $C_{15}H_{17}ON_5S$ requires N, 22·29 per cent.).

1 - o - *Tolylcarbohydrazide-5-thiocarbo-o-tolylamide*, m.p. 189°. (Found: N, 21·42. $C_{16}H_{19}ON_5S$ requires N, 21·27 per cent.).

1 - o - *Tolylcarbohydrazide-5-thiocarbo-p-tolylamide*, m.p. 213°. (Found: N, 21·19. $C_{16}H_{19}ON_5S$ requires N, 21·27 per cent.).

1-o-*Tolylcarbohydrazide-5-thiocarbo*-1:3:4-*xylylamide*, m.p. 186°. (Found: N, 20·52. $C_{17}H_{21}ON_5S$ requires N, 20·40 per cent.).

1 - o - *Tolylcarbohydrazide - 5 - thiocarboallylamide*, m.p. 197°. (Found: N, 25·19. $C_{12}H_{17}ON_5S$ requires N, 25·09 per cent.).

1-o-*Tolylcarbohydrazide-5-thiocarbo-β-naphthylamide*, m.p. 94–96°. (Found: N 19·25. $C_{19}H_{19}ON_5S$ requires N, 19·17 per cent.).

2-*Keto-5-phenylimino*-2:3:4:5-*tetrahydro*-1:3:4-*thiodiazole* (XI).

(*a*) Phenylcarbohydrazide-5-thiocarbophenylamide (5 g.) on being heated with strong hydrochloric acid (50 c.c.) under reflux on a water-bath for an hour went into solution with the separation of a tarry mass which solidified on cooling. The solid was crystallised twice from acetone, m.p. 246°. It is insoluble in acids and alkalis. (Found: N, 21·82. $C_8H_7ON_3S$ requires N, 21·76 per cent.).

The hydrochloric acid solution after cooling yielded a precipitate which was proved to be phenylhydrazine hydrochloride by preparing the benzaldehyde derivative.

(*b*) Phenylcarbohydrazide-5-thiocarbophenylamide (5 g.) suspended in water was heated with an excess of ferric chloride solution for an hour on a water-bath, when a tar-like substance was obtained which solidified on cooling. It was filtered, washed with water and triturated in a mortar with dilute alkali. The insoluble substance was again filtered, washed with water and crystallised thrice from alcohol, m.p. 246° (yield 1 g.). It was insoluble in acids and alkalis and was found to be identical with the above compound.

2-*Phenylhydrazino-5-anilino*-2:3:4:5-*tetrahydro*-1:3:4-*oxdiazole* (XII).—Phenylcarbohydrazide-5-thiocarbophenylamide (5 g.) was heated with 20% potassium hydroxide (about 40 c.c.) on a water-bath for about an hour and a half. At first it went into solution, then a precipitate came out which was washed with water and crystallised from acetic acid, m.p. 244—245° (yield 1 g.). It is insoluble in acids and alkalis. (Found: N, 26·4. $C_{14}H_{13}ON_5$ requires N, 26·21 per cent.).

Action of strong Hydrochloric Acid or Ferric Chloride upon 1-*Phenylcarbohydrazide-5-thiocarbo-o-tolylamide*: *Formation of* 5-*Tolylamino-2-keto*-2:3-*dihydro*-1:3:4-*thiodiazole*.—The method of treatment and isolation of the reaction product was the same as in the

case of the corresponding phenyl compound. The substance was insoluble in acid and alkali and was twice crystallised from alcohol, m.p. 220—221°. (Found: N, 20·32. $C_9H_9ON_3S$ requires N, 20·29 per cent.)

Treatment with ferric chloride under the aforesaid conditions resulted in the formation of an identical compound.

Most of the experimental work of this paper was done in the Chemical Laboratory of the Dacca University.

Our thanks are due to Prof. J. C. Ghosh for the kind interest he has taken in this work.

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Vegetable Proteins. Part II. Typhoidin—the Alcohol-Soluble Protein of *Pennisetum Typhoideum*.

By D. Narayanamurti and C. V. Ramaswami Aiyar.

Cumbu (*Pennisetum typhoideum* ; Tamil name, Cumbu; Telugu, Sajjalu; Hindustani, Bajra), a staple food of a considerable proportion of the Indian cultivating classes, occupies the fourth place among the grain crops of India and is cultivated over an area of 16 million acres (*Dept. Com. Int. & St., India*, 1928, 25). It is purely a rain-fed crop and is largely grown along with *Cajanus Indicus* or pigeon pea. It is highly resistant to drought and in nutritive value compares favourably with other Indian cereals.

As the cereal enters into the diet of large classes of people, a biochemical examination of it has been undertaken in order to assess its nutritive value. The present communication is concerned with a chemical study of the main protein in the grain.

Experimental.

The grain used in this investigation was obtained from the Koilpatti Agricultural Station (Madras). It was sun-dried and ground to a fine meal (40-mesh) which had the following composition: moisture, 7·92% ; ash, 2·34% ; ether extractives, 6·3% ; crude protein, 9·27% ; crude fibre, 2·3% ; carbohydrates (by difference), 71·87%. The ratio of husk to grain was about 8.

As will be seen the meal contains nearly 10% of protein and a rather characteristically large proportion of ether extractives. The finely ground meal was dried in large desiccators under vacuum and preserved in glass stoppered bottles.

Distribution of Nitrogen in the Meal.—To ascertain the distribution of nitrogen in the meal it was extracted successively with different solvents and the nitrogen extracted determined by Kjeldahl's method in the clear extracts. The results were as follows: water, 13·04% ; 6% sodium chloride, 8·69% ; 70% cold ethyl alcohol, 33·27% ; 70% hot ethyl alcohol, 6·95% ; 0·04% sodium hydroxide, 9·06%. 71% of the nitrogen in the meal has been accounted for

and it may be possible by repeated extraction with the above named solvents to account for nearly 90-95% of the nitrogen in the meal. It should be noted that more than 50% of the extractable nitrogen comes in the alcoholic extract, suggesting that most of the protein is the one usually known as ' prolamin.' As this forms the major portion of the protein in the cereal it formed the first object of the study.

Optimum Conditions of Extraction of the ' Prolamin.'

Mode of Extraction.—The first point to be investigated was the mode of extraction. Equal quantities of the meal were treated as follows (duration of extraction same): (*a*) stirring and filtering, (*b*) shaking and filtering, and (*c*) shaking and centrifuging. Aliquots of the extracts gave the following percentages for nitrogen extracted: (*a*) 32·4, (*b*) 32·4 and (*c*) 26·7. So in the subsequent experiments (*b*) was the mode of extraction adopted.

Influence of Concentration of Alcohol.—The next point to be investigated was the influence of concentration of the alcohol used. To 5 g. of the vacuum-dried meal were added 50 c.c. of ethyl alcohol of varying concentration and shaken for two hours at room temperature (25°). After filtration nitrogen in the extract was determined. The results are given in Table I.

TABLE I.

Concentration (by vol.)	Nitrogen extracted.	Concentration (by vol.)	Nitrogen extracted.	Concentration (by vol.)	Nitrogen extracted.
0%	15·21%	40%	7·02%	70%	31·97%
10	10·24	50	7·14	75	30·42
20	8·69	60	23·9	80	29·54
30	7·64	65	30·9	90	28·43

It is evident from the results that 70% alcohol is most suited for extraction. This may probably be due to the fact that the protein in the seed can be separated into two fractions: one water-soluble—the so-called ' globulin,' and the other peptisable by a mixture of water and alcohol—the ' prolamine ' (see, however, Gortner, *Kolloid Z.*, 1928, **44**, 97, on the inadequateness of the present classification). One has also to take into account the influence of such various factors as viscosity, surface tension, solvation, dipolemoment, association, etc., when dealing with peptisation by mixed solvents. Ostwald (*Kolloid Z.*, 1928, **45**, 56,331) has drawn attention to the great rôle

played by dipolemoment in such phenomena, and Jirgensons (*Kolloid Z.*, 1929, **47**, 236) has published some interesting experiments on the coagulation of strongly solvated sols with organic substances and water. He found that alcohols *sensitised* in presence of salts when the concentration of the alcohol was low but they acted as stabilisers in higher concentrations. A similar behaviour is noticeable here. Ethyl alcohol acts as a sensitiser up to a concentration of 60% and thereafter acts as a stabiliser. The meal used for the extraction of the protein contains 2·3% of ash and hence it is quite conceivable that the process is akin to that observed by Jirgensons. However we shall report in a subsequent paper a detailed experimental investigation of this question.

Influence of Period of Extraction.—Having studied the influence of concentration of the alcohol, the effect of period of extraction was examined. The results are given in Table II.

TABLE II.

Period of extraction.	Nitrogen extracted.	Period of extraction.	Nitrogen extracted.
1 hr.	31·28%	4 hrs.	32·15%
3 hrs.	33·09	5½ hrs.	32·15
3½ hrs.	32·15		

Three hours gave the best results and was finally adopted for the preparation of the protein. The lower amount of nitrogen extracted for longer periods may probably be due to denaturation of the protein.

Influence of the Quantity of Meal taken.—Much stress has been laid by Ostwald and collaborators (*Kolloid Z.*, 1927, **41**, 163; **43**, 249) on the rôle of the quantity of the solid phase in 'colloid solubility'. So the influence of the quantity of the meal taken on the nitrogen extracted was tried. The results are given in Table III.

TABLE III.

Quantity of meal taken (g.).	5	12·5	15	20	22·5
Nitrogen extracted (g.).	0·21515	0·47532	0·5847	0·7372	0·80635
Nitrogen extracted (percentage).					
1st extraction	34·33	34·57	32·46	30·66	29·67
2nd extraction	5·66	3·30	4·49	4·46	4·64
3rd extraction	3·04	1·74	2·03	1·74	1·55
Total	43·03	39·61	38·98	36·86	35·86

The results indicate that the quantity of nitrogen extracted increases with the quantity of the solid phase. If the percentage of nitrogen extracted is taken into account for a single extraction the maximum is attained when the ratio of meal to solvent is 1:4. If the sum of three consecutive extractions is considered then the maximum percentage is attained with the least quantity of the solid phase.

Preparation of Typhoidin

Several batches of 200 g. of the meal were extracted with 800 c.c. of 70% alcohol at room temperature in glass stoppered bottles for three hours. The extract was filtered under suction and the filtrate was concentrated under reduced pressure at 40-45° keeping the concentration of alcohol constant by addition of alcohol now and again, thus preventing the precipitation of the protein during concentration. The concentrated extract was poured into 20 litres of distilled water contained in tall glass cylinders under constant stirring when a milky suspension was obtained. To this a saturated solution of pure sodium chloride was added and the contents let stand for two days. During this period the protein had settled to the bottom of the cylinder. The supernatant liquid was syphoned off and the turbid bottom liquid centrifuged. The protein was washed on the centrifuge several times with distilled water to remove sodium chloride. It was then dissolved in hot 75% alcohol and reprecipitated. This process was again repeated. The protein so prepared was pressed between filter papers and dried in a vacuum desiccator. The powdered material was extracted with ether to remove ether-soluble impurities, dried in *vacuo* and powdered. The yield of pure product was about 30 g. per kg. of meal taken. The purity of the preparation was tested by estimation of nitrogen in different preparations which was found to be identical. The protein thus prepared was a light grey powder mostly soluble in 75% alcohol. It contains sulphur but no phosphorus.

Elementary Composition of Typhoidin.—Elementary analysis of the protein gave the following results (Table IV).

TABLE IV.

Element.	Percentage. I	Percentage. II	Average.
Carbon	56·4	57·18	56·79
Hydrogen	5·48	5·65	5·565
Nitrogen	15·3	15·3	15·3
Sulphur	0·61	0·60	0·605
Oxygen (by diffe).	22·21	21·27	21·74

Nitrogen was estimated according to Kjeldahl, carbon and hydrogen by combustion and sulphur according to Trotman and Bell (*J. Soc. Chem. Ind.*, 1926, **45**, 12).

Nitrogen Distribution in Typhoidin.—About three g. of the protein were hydrolysed by boiling under reflux with five parts of 25% hydrochloric acid till the liquid no longer gave any biuret reaction. It was found that 30 hours were sufficient. The hydrolysate was evaporated in *vacuo* to a stiky mass to remove hydrochloric acid. To the residue ammonia-free water was added and again concentrated in *vacuo*. The dry residue was now taken up with water and made up to 200 c.c. The nitrogen in the insoluble residue was determined according to Kjeldahl and was taken to represent acid-insoluble humin.

The filtrate was used for the estimation of nitrogen distribution according to Van Slyke, due regard being paid to all the improvements suggested by Plimmer and Rosedale (*Biochem. J.*, 1925, **19**, 1004 ; Daft, *Biochem. J.*, 1929, **23**, 149). Arginine was estimated in the hydrolysate after removal of amide nitrogen as also the acid soluble melanin nitrogen according to Plimmer (*Biochem. J.*, 1916, **10**, 115), adopting however the apparatus of Linderstrm-Lang (*Compt. rend. Carlsberg*, 1927-29, **17**, No. 9, 25). Plimmer has drawn attention to the fact that the arginine is not completely precipitated by phosphotungstic acid and the discrepancy noticed between the direct estimation in the hydrolysate and that in the basic fraction was easily accounted for by the arginine nitrogen in the mono-amino-fraction. The results are given in Table V.

TABLE V.

Nitrogen distribution in typhoidin (percentages of total nitrogen).

Form of nitrogen.	Percentage.	
Amide	21·31	
Humin :	2·59	
Insoluble		1·63
Soluble		0·96
Basic :	10·23	
Arginine		4·55
Histidine		2·49
Cystine		1·80
Lysine		1·39
Non-Basic :	64·66	
Amino		63·51
Non-amino		1·15
Total	98·79	

TABLE V*a*.

Nitrogen distribution of typhoidin as compared with that of other prolamins.

Form of nitrogen.	Typhoidin from *Pennisetum typhoideum.*	Gliadin from *Triticum vulgare.*	Eleusinin from *Eleusinin corocana.*	Sorghumin from *Sorghum vulgare.*	Zein from *Zea mais.*
Amide	21·31	25·52	20·52	18·96	18·06
Humin	2·59	0·87	1·17	3·08	1·11
Basic :					
Arginine	4·55	6·38	2·60	4·83	3·92
Histidine	2·49	5·41	2·69	1·19	2·45
Cystine	1·80	1·68	—	0·92	0·98
Lysine	1·39	0·57	0·64	3·45	0·89
Non-basic :					
Amino	63·51	53·49	69·03	60·01	66·08
Non-amino	1·15	6·14	2·13	5·33	5·90
Total	98·79				

Essential Amino-acids.—In order to correctly judge the nutritive value of the protein, accurate analysis of the essential amino-acids should be made. Cystine figures obtained by Van Slyke's method are incorrect—being racemised during hydrolysis it is incompletely precipitated by phosphotungstic acid. It was therefore estimated according to the methods of Sullivan (*J Biol. Chem.*, 1927, **75**, 14) and of Folin and Looney (*J. Biol. Chem.*, 1922, **51**, 421). Tryptophan was estimated colourimetrically according to Folin and Looney (*J. Biol. Chem.*, 1922, **51**, 421). Tyrosine was estimated according to Zuwerkalow (*Z. Physiol. Chem.*, 1926, **163**, 185) as also according to Folin and Looney (*J. Biol. Chem.*, 1922, **51**, 421). The results are given in Table VI.

TABLE VI.

Percentages of the essential amino-acids in typhoidin and other prolamins determined by different methods.

Amino-acid.	Typhoidin.	Eleusinins.	Gliadin.	Zein.	Method.
Arginine	2·19	2·23			Van Slyke
Histidine	1·42	1·13			"
Lysine	1·12	0·46			"
Cystine	1·81	1·39	2·32	0·50	Folin and Looney
"	1·52				Sullivan
Tyrosine	2·82	2·98			Zuwerkalow
"	2·49				Folin and Looney
Tryptophane	2·77		3·4	5·52	Folin and Looney
"		1·59			Koom.
"			1·14	0	

It is clear from the tables that typhoidin is not lacking in essential amino-acids. It compares favourably with other cereals in regard to the basic nitrogen it contains. It is similar to sorghumin but essentially superior to eleusinin. Its cystine content is higher than that of the other prolamins. The cystine content of typhoidin does not account for all the sulphur in the protein. This suggests that probably another sulphur containing amino-acid is present.

This point is receiving our attention. It is rich in tryptophane and it is therefore evident that it should be of high nutritive value if supplemented by a protein like cajanin which is deficient in this essential amino-acid but contains useful amounts of the diamino-acids.

Summary.

The chief protein in *Pennisetum typhoideum* is a prolamin which accounts for 43% of the total nitrogen.

The optimum conditions of extraction of the protein have been studied and the possible mechanism of protein peptisation by mixed solvents discussed.

The nitrogen distribution in the protein has been studied and the essential amino-acids determined.

It is characterised by a high content of cystine and tryptophane. The sulphur content suggest the presence of another sulphur-containing amino-acid.

The nutritive value of the protein has been discussed.

One of us (D.N.) is indebted to the Senate of the Indian Institute of Science for the award of a Research Studentship which enabled him to take part this investigation.

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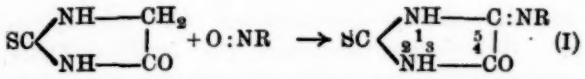
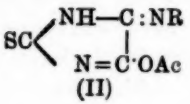
Dyes Derived from Thiohydantoin. Part I.

By Gajanan Purushottam Pendse and Sikhibhushan Dutt.

It has been observed in this laboratory that the intensely coloured condensation products from thiohydantoin and aromatic aldehydes may be used for the dyeing of woolen and silk fabrics. In course of the present investigation, it has been found that thiohydantoin also condenses with aromatic nitroso- and *iso*nitroso-compounds in presence of glacial acetic acid or acetic anhydride forming products (I) which are even more coloured than those obtained with aldehydes.



With acetic anhydride as the condensing agent, unstable acetyl derivatives, presumably of the type (II), are generally formed, which are however very easily hydrolysed by dilute alkalis (or by boiling water) to the free keto-types (I).



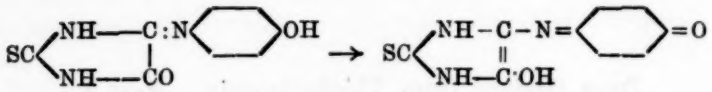
(II)

On account of the difficulty of purification of the acetyl derivatives due to their unstable nature, the condensation products described in this paper have been isolated only in the free keto-forms (I).

The condensation of thiohydantoin with *iso*nitroso-compounds (like *iso*nitrosocamphor, benzilmonoxime, etc.) may be explained by the assumption that these are at first converted into true nitroso-compounds by the migration of a hydrogen atom and then the condensation takes place in the usual manner.

If to the alcoholic solution of these dyestuffs a little caustic soda is added, the colour in many cases is considerably intensi-

fied. This behaviour is due to the possibility, which they possess, of passing into the quinonoid forms, thus:



In cases where the formation of the quinonoid structure is not possible, the colour change is not very marked, and there the enolisation may be supposed to take place as already explained.

The following nitroso- and *iso*nitroso-compounds have been condensed with thiohydantoin, and the products isolated in pure form, and described in the experimental portion in the same order: (1) nitrosobenzene, (2) *p*-nitrosophenol, (3) nitroso-β-naphthol, (4) nitrosothymol, (5) nitrosoresorcinol, (6) *p*-nitrosodimethylaniline, (7) *p*-nitrosodiethylaniline, (8) phenylmethylnitrosamine, (9) phenylethylnitrosamine, (10) nitrosodiphenylamine, (11) nitrosophenyl-α-naphthylamine, (12) nitrosophenyl-β-naphthylamine, (13) nitrosomethyl-β-naphthylamine, (14) nitrosocarbazole, (15) nitrosodimethyl-*m*-amidophenol, (16) nitrosodiethyl-*m*-amidophenol, (17) nitrosophenylhydroxylamine, (18) *iso*nitrosocamphor, (19) *iso*nitroso-1-phenyl-3-methylpyrazolone, (20) violuric acid, (21) benzilmonoxime and (22) phenanthraquinonemonoxime. Unsuccessful attempts were also made to condense the following aliphatic nitroso- and *iso*nitroso-compounds with thiohydantoin: nitrosomethylurethane, *ter.*-nitrosobutane and *iso*nitrosomethylethylketone. From this it seems that aliphatic compounds do not take part in the reaction. Most of the condensation products that have been isolated are crystalline substances, and they dye beautiful shades on wool and silk from a bath rendered slightly alkaline with borax or ammonium carbonate. They also dye cotton from a soda-bath (2% Na_2CO_3) in shades which are somewhat weaker than in the preceding cases.

Experimental.

5-Phenyliminothiohydantoin.—A mixture of thiohydantoin (2·5 g.), nitrosobenzene (2·2 g.) and acetic anhydride (15 c.c.) was heated under reflux on a sand-bath for 45 minutes. The reaction which was very vigorous at first, gradually subsided, and it was complete when the original dark green solution finally assumed a deep brownish-yellow shade. The mixture was allowed to cool and then

poured into water, when a brown precipitate came down. This was filtered off, washed with hot water, dissolved in warm dilute caustic soda and reprecipitated with dilute hydrochloric acid. Finally it was crystallised from alcohol in fine stout prisms with a nut-brown colour.

Condensations of thiohydantoin with the rest of the nitroso- and *iso*nitroso-compounds were similarly carried out with only slight modifications to suit individual cases. For the sake of abbreviation the properties of these compounds have been summarised in tabular form.

TABLE I.

Condensations of Thiohydantoin with Nitroso-Compounds.

	Name. (Iminothiohydantoin = H)	Appearance.	M.p.	Shade on wool and silk.	Wave-length of absorption maxima.	Analyses (Theoretical values in brackets).
(1)	5-Phenyl-H	Nut-brown prisms	Above 300°	Nut-brown	4845	S, 15·2% (15·6)
(2)	5-*p*-Hydroxyphenyl-H	Chocolate-brown prisms	,,	Light chocolate	4900	14·6% (14·5)
(3)	5-(2)-Hydroxynaphthyl-H	Yellow-brown ,,	184°	Light brown	4190	11·5% (11·8)
(4)	5-(3) *iso*Propyl-4′-hydroxy -6-methylphenyl-H	Reddish-brown Crystalline powder	Above 300°	Yellow	4280	11·2% (11·55)
(5)	5-(1′ :3′-Dihydroxy) phenyl-H	Dark brown crystalline-powder.	278°	Deep chocolate	4470	13·8% (14·2)
(6)	5-(*p*-Dimethylamino)phenyl-H	Reddish-brown needles	212°	Brownish-red	4610	12·4% (12·8)
(7)	5-(*p*-Diethylamino)phenyl-H	,, ,, ,,	162°	,, ,,	4690	11·4% (11·6)
(8)	5-Phenylmethylamino-H	Yellow-brown ,,	156°	Light brown	4600	13·4% (13·2)
(9)	5-Phenylathylemino-H	,, ,, ,,	174°	,, ,,	4650	13·2% (12·9)
(10)	5-Diphenylamino-H	Brown powder	191°	Dark tan	4880	10·7% (10·81)
(11)	5-Phenyl-α-naphthylamino-H	Brown needles	Above 300°	Light tan	4210	9·6% (9·53)
(12)	5-Phenyl-β-naphthylamino-H	Light brown needles	,, ,,	Yellow-brown	3940	9·8% (9·53)
(13)	5-Methyl-β-naphthylamino-H	Light chocolate ,,	,, ,,	,, ,,	4020	11·6% (11·3)
(14)	5-*N*-Carbazole-H	Reddish-brown powder.	,, ,,	Terra cota	4670	10·98% (10·88)
(15)	5-(β-Dimethyl-*m*-amino) phenyl-H	Orange-brown needles	,, ,,	Cold sepia	4390	12·4% (12·1)
(16)	5-(*p*-Diethyl-*m*-amido) phenyl-H	Reddish-brown needles	,, ,,	Warm sepia	4420	11·4% (11·0)
(17)	5-Phenylhydroxylamino-H	Brownish-yellow powder	,, ,,	Yellow-brown	3870	13·3% (13·56)

TABLE II.

Condensations of Thiohydantoin with iso*Nitroso-Compounds.*

(18)	5-Camphoryl-H	Brownish-yellow powder	Above 300°	Yellow-brown	4350	S, 11·7% (11·4)
(19)	5-(2-Methyl-4-phenyl-5-keto)-dihydro-pyrazole-H	Chocolate brown powder	,, ,,	Chocolate-brown	4570	11·0% (10·63)
(20)	5-Carbamidomalonyl-H	Deep chocolate powder	,, ,,	Dark tan	4960	12·2% (12·5)
(21)	5-Diphenylenthanol-H	,, ,,	,, ,,	Orange-brown	4680	9·4% (9·9)
(20)	5-(9)-Phenanthrol-H	,, ,,	,, ,,	Brownish-red	4990	9·6% (9·9)

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A Note on the Complexity of the Magnetic Properties of Elements in the Colloidal State.

By S. S. Bhatnagar.

The magnetic properties of elements, in the colloidal state, have been investigated in only a few cases. Honda (*Ann. Physik*, 1910, *iv*, **32**, 1027) and Owen (*ibid*, 1912, *iv*, **37**, 657), were the first to investigate colloidal bismuth and show that it is about one third as diamagnetic as the metal crystals. Results in the same direction have recently been obtained by Vaidyanathan (*Nature*, 1930, **125**, 672 and *Indian J. Phys.*, 1930, **5**, 559) in the case of graphite, bismuth and antimony. The influence of crystalline structure on the magnetic properties of elements is well known from the work of Faraday and Tyndall, but generally the effects are of a much smaller order of magnitude than those obtained in the case of the above-named elements. It, therefore, appeared desirable to exclude the following possibilities before accepting the proferred explanation of this effect.—(1) The adsorption of gases from the atmosphere. (2) The formation of the oxide on the surface when the substance is powdered to colloidal dimensions. Powdered bismuth, as well as colloidal bismuth, prepared by Bredig's method, were therefore tested for the presence of the oxide by Muir's test (*J. Chem. Soc.*, 1877, **31**, 658) and found to contain quite appreciable amounts of it. The melting points of the powder and colloidal bismuth were also found to be different from that of the metal.

It now remained to examine whether the oxides of bismuth were sufficiently paramagnetic or much less diamagnetic than the metal itself, to account for a part of the observed changes in diamagnetism. BiO was therefore prepared by Mr. Mulkh Raj according to Schneider's method (*Ann. Phys. Chem.*, 1853, **88**, 45). This substance is extremely unstable excepting when in solution with the metal, as is the case with many other suboxides. The susceptibility of this very wet powder was determined by Mr. R. N. Mathur, M.Sc. by the Interference Balance (Phil. Mag., 1929, *vii*, **8**, 1041). It was found to be very feebly diamagnetic, and if the susceptibility of water present be

accounted for, it might leave the black residue slightly paramagnetic. That BiO should be paramagnetic is also clear from the fact that it is a compound with an odd molecular number. Besides Williams (*Physical Rev.*, 1926, *ii*, **28**, 167) has shown that BiO_2 is definitely paramagnetic and the presence of this material has not been excluded in previous investigations on colloidal bismuth.

In order to show further that the tarnishing of the surface is of enough consequence, a piece of the metal was dipped in dilute nitric acid, so that a black tarnish was formed on its surface. This piece was then washed with water to remove any soluble nitrates, etc. and the specific susceptibility of the tarnished metal was found to be much less than that of the pure metal.

It is, therefore, necessary to be cautious in advancing views regarding anomalous diamagnetism of substances on powdering or colloidisation. From the study of steel, it is abundantly clear that small amounts of chemical substances, which form solid solution with iron, play an important part in the magnetic properties of steel and hence the laws that govern the change of magnetic properties in solid solutions should be discovered before any definite conclusions could be arrived at. From our experiments, it is clear that at least a good part of the effect in bismuth is due to the formation of the black oxide.

The investigation of copper and other elements of its family is also very important in this connection. Unlike bismuth and antimony, their susceptibilities increase on melting. Moreover, while the atoms of Cu, Ag and Au are paramagnetic according to the experiments of Stern and Gerlach, the metal crystals are diamagnetic. In such cases diamagnetism should, therefore, increase if powdering alone is of any consequence.

Experiments on the thermal, chemical and colloidal changes of diamagnetism of the above elements are in progress and the results will shortly be communicated for publication. We are also investigating as to how the susceptibility of a diamagnetic or a paramagnetic substance varies when it is coated all over the surface with a paramagnetic or a diamagnetic material respectively.

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LAHORE.

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A Note on the Percentage of Iodine in certain Algae.

By S. C. Dixit.

Working on Indian sea-weeds the author found in 1928 that (*a*) the algæ which supply the bulk of the material for the iodine industry in Europe, *viz.*, *Laminaria*, *Fucus serratus* and *Chorda filum*, are absent from Indian waters, and (*b*) the time for the harvest of sea-weeds was confined to the cold weather. The weed is used as a manure, *e.g.*, for cocoanut trees.

In the winter (February-March) of 1929 the author collected a a large amount of different species of algæ from various places of the Bombay Presidency from the drift-weed along the shore line. The percentage of iodine calculated for the dry weed (natural drying in air) is recorded below. (For method, see Stanford, *Chem. News*, 1877, **35**, 172).

Weed.	Iodine (%).	Place.
Fucus.*	0·027	Porbundar.
Sargassum*	0·032	,,
,,	0·034	Bombay (Juhu).
,,	0·049	Okha.
Asparogopsis sansfordiana.	0·092	,,
Halymenia.*	0·035	,,
Gracilaria*	0·023	,,

* Species not determined.

Of the above genera *Sargassum* (*ginbaso*), used for the iodine industry in Japan, has been reported by Smith (*Bureau Fisheries Bull.*, 1909, **24**, 162) to yield 0·054% and 0·029% of iodine from two localities. The percentage of iodine observed by the author compares favourably with the results of weeds from other countries. The practical difficulties facing its industrial use are twofold, *viz.*, collection, and lack of sufficient quantity of weeds throughout the year.

My thanks are due to my friend Mr. J. S. Vaidya for his interest in the work and particularly the chemical side of it.

Wilson College, Bombay. *Received November 17, 1930.*

Thiodiazines. Part VII. Condensation of Ethyl Chloroacetate with Thiosemicarbazides.

By Prafulla Kumar Bose and Birendra Kumar Nandi.

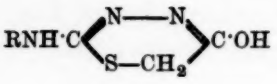
Some derivatives of 5-hydroxythiodiazines have previously been obtained by Bose (*J. Indian Chem. Soc.*, 1926, **3**, 148) and by Guha and Roy-Choudhury (*J. Indian Chem. Soc.*, 1928, **5**, 153) who showed that condensation of substances of the type R′·C(SH) $=N\cdot NH_2$ (where R′ = S-alkyl or PhNH·NH—) with α-halogenated aliphatic esters in presence of suitable condensing agents led to the formation of hydroxythiodiazines.* This reaction has now been extended to thiosemicarbazide and 4-substituted thiosemicarbazides, which are structurally analogous to those substances that have already been employed for the synthesis of 1:3:4-thiodiazines.

The reaction between ethyl chloroacetate (or the acid) and thiosemicarbazides is not as energetic as that between a thiosemicarbazide and an halogenated ketone, and the yield, though good, is not quantitative. Condensing agents like pyridine or alcoholic alkali appear to influence the velocity of the reaction as also the yield, but not to a considerable extent. The reactions have been carried out mainly in absence of any condensing agent, as this procedure gave a cleaner product.

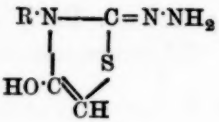
The high-melting crystalline products of condensation may be represented by the general formula (I) which agrees with the observed properties. They dissolve in warm aqueous alkalis as also in acids, and yield monoacetyl derivatives on acetylation in the usual manner. They could not be desulphurised by freshly prepared yellow mercuric oxide or alkaline lead oxide—a test which is employed for the orientation of a sulphur atom in heterocyclic compounds. It was further concluded, on account of the indifference of the compounds towards ketones and aldehydes, that they do not carry any

* There appears to be some anomaly regarding the thiodiazine constitution assigned to the compound (XXVI) of Guha and Roy-Choudhury (*ibid*, p. 154). The benzylidene derivative of this compound should be expected to be identical with their compound (XXIX) but they are reported to have different properties.

hydrazino-group, as might be expected if the products had the thiazole constitution (II), which is isomeric with (I) (*cf.* Besthorn, *Ber.*, 1910, **43**, 1523).



(I)



(II)

The monoacetyl derivatives, with the exception of that derived from the compound (I, R=H), as also the methyl derivatives are also insoluble in alkalis.

Experimental.

General Method.—Molecular proportions of the thiosemicarbazide and ethyl monochloroacetate were dissolved in alcohol (dilute, in the case of unsubstituted thiosemicarbazide) and heated under reflux on a water-bath for about an hour. The crystalline condensation product separated out during the progress of the reaction. The mother-liquor usually gave on standing overnight or on further heating a second crop. The substance was purified by crystallisation from suitable solevnts.

Acetylation.—The acetylation was carried out by boiling the compounds with an excess of acetic anhydride and a drop of pyridine for 15–20 minutes.

Methylation.—A mixture of the hydroxythiodiazine (1 mol.), methyl iodide (little more than 1 mol.) and methyl alcoholic potassium hydroxide (1 mol.) solution (1 per cent.) was boiled under reflux for 6-7 hours on the water-bath. The contents were then filtered and the brown filtrate evaporated to dryness at the room temperature, when a solid residue was usually obtained. This was collected, dried over porous plate to remove some adhering oil and crystallised.

2-Amino-5-hydroxy-1:3:4-thiodiazine.—It was obtained from ethyl monochloracetate (or the acid) and thiosemicarbazide in about 70 per cent. yield. The product was extracted with boiling water to remove unaltered thiosemicarbazide and finally crystallised from a mixture of alcohol and pyridine in colourless prisms. It is easily soluble in acetone and pyridine but only sparingly in alcohol. It decomposes and melts at 284°. (Found: N, 32·17. $C_3H_5ON_3S$ requires N, 32·06 per cent.).

This substance is probably identical with that obtained by Harries and Klamt (*Ber.*, 1900, **33**, 1152) from hydrazine and thiocyanacetic acid.

The *acetyl* derivative separates from alcohol as needleshaped crystals melting at 205°. (Found: N, 24·21. $C_5H_7O_2N_3S$ requires N, 24·13 per cent.)

The *benzoyl* derivative, obtained in the usual manner, crystallised from alcohol and melted at 260°. (Found: N, 17·59. $C_{10}H_9O_2N_3S$ requires N, 17·87 per cent.)

2-Amino-5-hydroxy-1:3:4-thiodiazine, like primary amines in general, formed an *additive* compound with phenylthiocarbimide. It separated from alcohol as light yellow needles, m.p. 195°. (Found: N, 20·85. $C_{10}H_{10}ON_4S_2$ requires N, 21·05 per cent.).

2-*Methylamino-5-hydroxy*-1:3:4-*thiodiazine* (I, R=Me).—It is sparingly soluble in alcohol, moderately in benzene, and easily in pyridine and acetic acid. It separated as colourless needles from a mixture of pyridine and alcohol; m.p. 282° with decomp. (Found: C, 32·95; H, 5·0; N, 29·08. $C_4H_7ON_3S$ requires C, 33·10; H, 4·83; N, 28·96 per cent.).

The *acetyl* derivative formed pale yellow needles, m.p. 198°. (Found: N, 22·40. $C_6H_9O_2N_3S$ requires N, 22·46 per cent.).

The *methyl* derivative, which was a brown oil, could not be obtained in a sufficiently pure condition.

2-*Ethylamino-5-hydroxy*-1:3:4-*thiodiazine* (I, R=Et).—2·5 G. of the product were obtained from 2·9 g. of ethylthiosemicarbazide and 3 g. of ethyl monochloracetate. It separated from acetic acid in colourless prisms melting at 225°. It is very soluble in pyridine but only sparingly in alcohol. (Found: C, 37·58; H, 5·49; N, 26·61. $C_5H_9ON_3S$ requires C, 37·70; H, 5·66; N, 26·41 per cent.)

The *acetyl* derivative crystallised in needles (alcohol) and melted at 169°. (Found: N, 20·80. $C_7H_{11}O_2N_3S$ requires N, 20·89 per cent.)

2-iso*Butylamino-5-hydroxy*-1:3:4-*thiodiazine* (I, R=iso*butyl*).—7·2 G. of *iso*butylthiosemicarbazide and 6 g. of ethyl monochloroacetate gave 4·3 g. of pure product. It is sparingly soluble in methyl or ethyl alcohol but moderately in pyridine, acetone, acetic acid and almost insoluble in benzene; m.p. 210°. (Found: N, 22·50. $C_7H_{13}ON_3S$ requires N, 22·46 per cent.).

The *acetyl* derivative formed light yellow needles from absolute alcohol; m.p. 199°. (Found: N, 18·27. $C_9H_{15}O_2N_3S$ requires N, 18·34 per cent.)

The *monomethyl* derivative separated as colourless needles from alcohol, m.p. 135°. It is easily soluble in acetone, sparingly in benzene and insoluble in chloroform. (Found: N, 21·03. $C_8H_{15}ON_3S$ requires N, 20·89 per cent.)

2-*Phenylamino-5-hydroxy*-1:3:4-*thiodiazine* (I, R=Ph).—The product, obtained in about 50 per cent. yield, was found to be very sparingly soluble in alcohol, and hot benzene but easily in pyridine, and acetic acid. It separated from the last named solvent as colourless needles, m.p. 184°. (Found: C, 51·9; H, 4·4; N, 20·18. $C_9H_9ON_3S$ requires C, 52·10, H, 4·3; N, 20·3 per cent.).

The *acetyl* derivative, a pale yellow crystalline compound, crystallised from alcohol and melted at 172°. (Found: N, 16·77. $C_{11}H_{11}O_2N_3S$ requires N, 16·87 per cent.).

The *methyl* derivative crystallised from alcohol in colourless needles, m.p. at 265°. (Found: N, 19·19. $C_{10}H_{11}ON_3S$ requires N, 19·00 per cent.).

2-o-*Tolylamino-5-hydroxy*-1:3:4-*thiodiazine* (I, R=o-*tolyl*).—It crystallised from pyridine in colourless needles, m.p. 188°. It is sparingly soluble in alcohol and benzene. (Found: N, 19·12. $C_{10}H_{11}ON_3S$ requires N, 19·00 per cent.).

The *acetyl* derivative formed light yellow needles, m.p. 210°. (Found: N, 15·90. $C_{12}H_{13}O_2N_3S$ requires N, 15·96 per cent.).

2-p-*Tolylamino-5-hydroxy*-1:3:4-*thiodiazine* (I, R=p-*tolyl*).—The substance was sparingly soluble in alcohol, benzene or acetone but easily in pyridine and acetic acid. It melted at 195° after crystallisation from pyridine. (Found: N, 18·91. $C_{10}H_{11}ON_3S$ requires N, 19·00 per cent.).

The *acetyl* derivative crystallised in pale yellow needles, m.p. 218°. (Found: N, 16·00. $C_{12}H_{13}O_2N_3S$ requires N, 15·96 per cent.).

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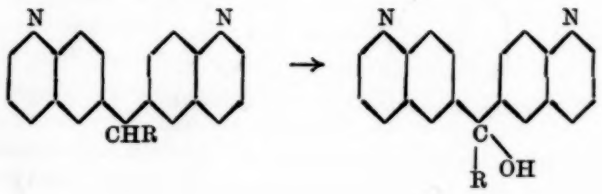
Triphenylmethane Dyes derived from Quinoline, Tetrahydroquinoline, Diphenylamine and Carbazole.

By Rajendra Nath Sen and Bhola Nath Sen.

Although the condensation of various aldehydes with aromatic amines has been previously investigated, that with quinoline appears to have been very little studied. Therefore it seemed to be of interest to undertake the investigation of the reaction between quinoline and various aldehydes with a view to make a comparative study of the products derived from it and those from tetrahydroquinoline, diphenylamine and carbazole.

It is now found that two molecules of quinoline condense with one molecule of an aromatic aldehyde in the presence of concentrated hydrochloric acid on the water-bath to produce a leuco-base (I) analogous in constitution to the leuco-base of malachite green, the carbinol compound (II) being obtained by oxidation with lead peroxide, thus:



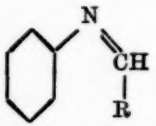
(I) (II)

The condensation with β-resorcyl aldehyde takes place most readily (yield, 70 per cent.). In these condensations the linking with the aldehydic carbon atom takes place in position 6, since when this position is occupied, as in 6-nitroquinoline, the reaction does not take place. It seems that an acidic group in the *meta*-position in the aldehyde molecule retards the reaction to a great extent: *m*-nitrobenzaldehyde reacts with extreme difficulty while *m*-hydroxy-

benzaldehyde does not react at all. Aliphatic aldehydes, like formaldehyde and cinnamic aldehyde, could not be condensed with quinoline.

Tetrahydroquinoline, which had been previously condensed with benzaldehyde and formaldehyde (Einhorn, *Ber.*, **19**, 1243, *Rec. trav. chim.*, 1906, **25**, 261), and *N*-methyltetrahydroquinoline have also now been condensed with various aldehydes with a view to compare their reactivities as well as the derived dyes with quinoline. It appears that the greater activity of tetrahydroquinoline and the stronger basic character of the compounds derived from it as compared with those of quinoline are due to the difference in configuration of the nitrogen atom in the two compounds, which forming part of a ring, is doubly linked in quinoline but singly linked in tetrahydroquinoline.

It is known that the reactivity of the hydrogen atom in the *para*-position to the amino-group is markedly increased if the latter is alkylated but is appreciably diminished when it is converted into -N:N- (as in azobenzene) or into -N:CH- group (as in benzylideneaniline). Tetrahydroquinoline may be compared to a secondary (alkylated) aromatic amine and quinoline to an amine, in which the amino-group has been changed into -N:CH-, and thus the feeble activity of the hydrogen atom in the *para*-position to the quinoline nitrogen atom may be accounted for.



Benzylidene aniline.

Quinoline.

For further study of the influence of the NH- and substituted NH-group on the reactivity of the *para*-hydrogen atom and on the basic character of the condensation products, diphenylamine, *N*-methyldiphenylamine, carbazole ond *N*-methylcarbazole have also been condensed with different aldehydes. The feeble reactivity of the *para*-hydrogen atom in diphenylamine and the week basic character of the compounds derived from it may be attributed to the phenylation of the amino-group but on methylation of the imino-hydrogen atom, the reactivity is increased to a remarkable extent although the basic character is slightly increased. Carbazole which was previously condensed with aldehydes in the presence of sulphuric

acid or zinc chloride (Dutt, *J. Chem. Soc.*, 1924, **125**, 502) condensed with benzaldehyde also in the presence of hydrochloric acid but less readily than diphenylamine, and the effect of methylation is not so marked as in diphenylamine; hence it appears that the influence of the NH-group is markedly affected when the nitrogen atom forms part of a ring.

A comparative study of the dyes derived from quinoline and tetrahydroquinoline shows that the tetrahydroquinoline complex exerts a stronger auxochromic influence than the quinoline complex and, therefore, although the dyes from tetrahydroquinoline are in a sense the reduction products of those from quinoline, yet they exhibit deeper shades as reduction causes the introduction of a stronger auxochrome (*cf.* indanthrene yellow which also gives a deeper colour (blue vat) on reduction.

A comparison of the influence of the auxochromic groups in the dyes derived from quinoline and tetrahydroquinoline is also interesting (*vide* Table IV). The condensation product of diphenylamine and benzaldehyde yields a disulphonic acid derivative, which, after oxidation, dyes silk and wool a green shade.

Experimental.

A. *Dyes derived from Quinoline.*

Phenyldiquinolylmethane.—A solution of pure synthetic quinoline (14 c.c.) dissolved in concentrated hydrochloric acid (37 per cent., 15 c.c.) and benzaldehyde (6 c.c.) is heated upon the water-bath for about 26 hours keeping the mouth of the flask open towards the end of the reaction. The product is extracted with 100 c.c. of water and made alkaline with caustic soda solution, when a light green product is obtained. The mixture is distilled in steam to free it from quinoline and benzaldehyde. The precipitate is washed with hot water, dissolved in dilute acetic acid and reprecipitated with ammonia, the process being repeated. The product is finally crystallised from a mixture of alcohol and acetic acid (1 : 1); yield, 30 per cent.

It is obtained as a light green powder readily soluble in acetic acid and nitrobenzene, fairly soluble in hot alcohol; insoluble in chloroform, carbon disulphide and benzene. The carbinol compound obtained by the oxidation of the leuco-base with freshly prepared lead peroxide, dyes wool, silk and tannined cotton a light green shade. (Found: N, 8·23. $C_{25}H_{18}N_2$ requires N, 8·09 per cent.).

Chloroplatinate.—0·2 G. of the leuco-base is dissolved in dilute hydrochloric and acetic acid (1:3) and 1 c. c. of platinic chloride (10%) is added when a precipitate is formed which is recrystallised from hot water in orange-yellow needles melting at 230° (decomp). (Found: Pt, 25·3. $(C_{25}H_{18}N_2)H_2PtCl_6$ requires Pt, 25·8 per cent.).

Picrate.—0·4 G. of the leuco-base, in 2 c. c. of glacial acetic acid, is heated upon the water-bath with an alcoholic solution of picric acid for 1 hour. The mixture is poured into water and the precipitate thus obtained is recrystallised from water in golden yellow spangles melting at 199°. (Found: N, 12·4. $(C_{25}H_{18}N_2)C_6H_2(NO_2)_3OH$ requires N, 12·17 per cent.)

Other triphenylmethane dyes derived from quinoline are described below:

TABLE I.

Name and formula.	Method of preparation. (Q = quinoline).	M.p. and appearance.	P. c. of N: Calc. and found.	Properties.
p-Methoxyphenyldiquinolylmethane, $C_{26}H_{20}N_2O$	Q + anisaldehyde + conc. HCl on water-bath for 20 hrs.	Yellow microcrystalline powder.	7·44; 7·46	Soluble in pyridine, acetic acid, mineral acids; insoluble in acetone, benzene and chloroform.
-Hydroxyphenyldiquinolylmethane, $C_{25}H_{18}N_2O$	Q + salicylaldehyde + conc. HCl on the water-bath for 26 hrs.	157-160°; yellow microcrystalline powder.	7·73; 7·76	Soluble in caustic alkalis, sparingly so in cold mineral acids, insoluble in alcohol, acetone and benzene.
p-Hydroxyphenyldiquinolyl methane, $C_{25}H_{18}N_2O$	Q + *p*-hydroxybenzaldehyde on water-bath + conc HCl for 26 hrs.	Does not melt below 263°; microcrystalline powder.	7·7; 7·0	Soluble in mineral and acetic acid, insoluble in benzene and chloroform.
o, *p*, *m*-Nitrophenyldiquinolylmethane, $C_{25}H_{17}N_3O_2$	Q + *o*, *p*, or *m*-nitrobedzaldehyde at 110-120° with conc. HCl for 17,10, 26 hrs. respectively.	108° of *p*-compound; *ortho* and *meta* compounds could not be isolated in a very pure form.	10·74; 10·74 (*ortho*) 11·2 (*meta*) 10·88 (*para*)	All the three are soluble in mineral and acetic acids and insoluble in benzene and acetone.

TABLE I—*continued.*

Name and formula.	Method of preparation. (Q = quinoline).	M.p. and appearance.	P.c. of N: Calc. and found.	Properties.
Dimethyl-*p*-aminophenyldiquinolylmethane, $C_{27}H_{23}N_3$.	Q + dimethyl-*p*-aminobenzaldehyde on water-bath with conc. HCl for 12 hrs.	168-170°; microcrystalline brown powder.	10·8; 11·9	Soluble in mineral and acetic acids and alcohol, insoluble in benzene and CS_2.
2:4-Dioxyphenyldiquinolylmethane, $C_{25}H_{18}N_2O_2$	Q + β-resorcyl aldehyde at 110° for 4 hrs. till the mixture assumes a deep violet colour with conc. HCl.	Does not melt below 240°; microcrystalline brown powder.	7·40; 7·37	Soluble in ammonia, caustic alkalis, alcohol and glacial acetic acid; insoluble in benzene and acetone.
(*a*) Monoacetyl derivative, $C_{27}H_{20}N_2O_3$	The carbinol compound + fused sodium acetate and acetic anhydride.	Decomposes without melting; microcrystalline brown powder.	6·66; 6·60	Soluble in caustic alkalis; insoluble in most organic solvents; gives a deep red colour with $FeCl_3$.
(*b*) Diacetyl derivative, $C_{29}H_{22}N_2O_4$	Q + β-resorcyl aldehyde + acetic anhydride and fused sodium acetate at 150-160°.	Does not melt below 267°; microcrystalline yellowish-brown powder.	6·06; 6·05	Soluble in glacial acetic acid; insoluble in alkalis, does not give coloration with $FeCl_3$.
(*c*) Disilver salt, $C_{25}H_{16}N_2O_2Ag_2$	Solution of the carbinol compound + alcoholic silver nitrate.	Red flakes.	Ag 36·5, 35·5	Crystallises from alcohol in red flakes.

B. *Dyes derived from Tetrahydroquinoline.*

m-*Hydroxyphenyl-ditetrahydroquinolylmethane.*—A mixture of tetrahydroquinoline (6 g.) *m*-hydroxybenzaldehyde (2·8 g.) and hydrochloric acid (25 c.c. of 20%) is heated on the water-bath for five hours. The mixture is made alkaline with dilute caustic soda solution, and is distilled in steam. The residue is dissolved in dilute hydrochloric acid and reprecipitated with ammonia and finally crystallised from alcohol. It is a microcrystalline, brown powder, soluble in mineral and acetic acids, in alcohol and acetone. It does not melt below 256°. The carbinol compound obtained by the oxidation of the leuco-base dyes wool and silk light brown shades. (Found: N, 7·42. $C_{25}H_{28}N_2O$ requires N, 7·52 per cent.).

Other triphenylmethane dyes derived from tetrahydroquinoline are given in Table II.

TABLE II.

Name and formula.	Method of preparation (T=tetrahydroquinoline)	M.p. and appearance.	P.c. of N : calc. and found.	Properties.
m-Nitro *p*-ditetrahydroquinolylmethane, $C_{25}H_{27}N_3O_2$	T + *m*-nitrobenzaldehyde on water-bath for 5 hrs. with 25% HCl.	212° (decomp.) ; lustrous green plates.	10·47 ; 10·8	Soluble in alcohol and acetone and insoluble in benzene.
Furfuryl-ditetrahydroquinolylmethane, $C_{23}H_{24}N_2O$	T + furfuraldehyde in alcohol on water-bath for 6 hrs. with 25% HCl.	Decomposes without melting ; dark brown micro-crystalline powder.	8·14 ; 7·94	Sparingly soluble in acids and alkalis, insoluble in most organic solvents.
p-Methoxyphenyl-ditetrahydroquinolylmethane $C_{26}H_{28}N_2O$	T + anisaldehyde with 25 % HCl on water-bath for 6 hrs.	Microcrystalline green powder.	6·29 ; 7·38	Dissolves in conc. sulphuric acid (giving a green solution with red fluorescence), alcohol (giving a green solution) and in glacial acetic acid.
o-Hydroxyphenyl ditetrahydroquinolylmethane, $C_{25}H_{26}N_2O$	T + salicylaldehyde on water-bath for 6 hrs. with 25% HCl.	163-164° ; microcrystalline yellow powder.	7·56 ; 7·90	Soluble in acids, insoluble in ether and acetone.
p-Hydroxyphenyl ditetrahydroquinolylmethane, $C_{25}H_{26}N_2O$	T + *p*-hydroxybenzaldehyde on the water-bath for 6 hrs. with 25% HCl.	255° ; greenish plates.	7·56 ; 7·22	Soluble in mineral acid giving a green solution with a red fluorescence.
Dimethyl-*p*-aminophenyl-ditetrahydroquinolylmethane, $C_{27}H_{31}N_3$	T + dimethyl-*p*-aminobenzaldehyde with 25 % HCl.	Semi-solid at the ordinary temperature, solid at 10°.	10·58 ; 10·92	Soluble in mineral and acetic acids and alcohol insoluble in benzene.
2 :4-Dioxyphenyl-ditetrahydroquinolylmethane $C_{25}H_{26}N_2O_2$	T + *p*-resorcyl aldehyde with 25% HCl.	Does not melt below 253° ; microcrystalline red powder.	7·25 ; 7·32	Soluble in alcohol, insoluble in benzene.
Di-*N*-methyltetrahydroquinolylmethane, $C_{21}H_{26}N_2$	T + *N*-methyltetrahydroquinoline + formaldehyde with 30 % HCl.	Microcrystalline brown powder.	9·15 ; 9·81	Soluble in acids alcohol and acetone, insoluble in benzene and chloroform.
Phenyldi-*N*-methyltetrahydroquinolylmethane, $C_{27}H_{30}N_2$	*N*-Methyltetrahydroquinoline + benzaldehyde with 25% HCl.	Sinters at 90°, melts at 100° ; yellow microcrystalline powder.	7·32 ; 7·30	Soluble in acetone and alcohol, insoluble in benzene and chloroform.

C. *Dyes derived from Diphenylamine and Carbazol.*

A mixture of diphenylamine (10 g.) dissolved in rectified spirit (30 c.c.), benzaldehyde (3 c.c.) and concentrated hydrochloric acid is heated upon the water-bath under reflux for 13 hours when a light green precipitate separates out. The product is washed repeatedly with boiling alcohol to remove any unaltered diphenylamine and benzaldehyde, dissolved in hot glacial acetic acid and poured into water when it is re-precipitated (yield, 50%). It is finally crystallised from a mixture of glacial acetic acid and absolute alcohol (2:1).

It is obtained as a green microcrystalline powder insoluble in most of the organic solvents except in nitrobenzene and hot glacial acetic acid and in concentrated sulphuric acid from which it is re-precipitated on dilution. When oxidised with lead peroxide in nitrobenzene solution and acetic acid a deep green product is obtained (Found: N, 6·76. $C_{31}H_{26}N_2$ requires N, 6·57 per cent.).

The Disulphonic Acid.—5 G. of the leuco-base are heated with 15 c.c. sulphuric acid (*d* 1·84) for 10 hours on the water-bath and poured into water when a brown precipitate is formed; it is washed with water and crystallised from alcohol in green plates soluble in water and alcohol. (Found: S, 10·6. $C_{31}H_{26}N_2S_2O_6$ requires S, 11·1 per cent.). When oxidised with lead peroxide it dyes wool and silk green shades.

TABLE III.

Dyes derived from Diphenylamine and Carbazole.

Name and formula.	Method of preparation.	M.p. and appearance.	P.c. of N: calc. and found.	Properties.
Dimethyldiphenyldiaminotriphenylmethane, $C_{33}H_{30}N_2$	*N*-methyldiphenylamine + benzaldehyde without any condensing agent upon water-bath for ½ hr.	144-146°; greenish microcrystalline powder.	6·14; 6·22	Soluble in pyridine and glacial acetic acid (1:1) and nitrobenzene.
Phenyl-dicarbazole methane, $C_{31}H_{22}N_2$	Carbazole + benzaldehyde on water-bath with conc. HCl for 13 hrs.	Does not melt below 260°; faintly green powder.	6·63; 6·40	Soluble in pyridine, hot acetic acid, conc. sulphuric acid; insoluble in ether, benzene and chloroform.
Phenyldi-*N*-methylcarbazole methane, $C_{33}H_{26}N_2$	*N*-methylcarbazole + benzaldehyde with conc. HCl.	Bluish-green microcrystalline powder; sinters at 140°, melts at 148°.	6·22; 6·36	Soluble in glacial acetic acid and nitrobenzene.
Diphenyldiaminotriphenylmethane, $C_{25}H_{22}N_2$	Diphenylamine + formaldehyde + conc. HCl on the water-bath for 12 hrs.	Bluish-green powder.	8·0; 8·37	Insoluble in most organic solvents; soluble in nitrobenzene.

TABLE III—*Continued.*

Name and formula.	Method of preparation.	M.p. and appearance.	P.c. of N: calc. and found.	Properties.
Diphenyldimethyldiaminodiphenylmethane, $C_{27}H_{36}N_2$	*N*-methyldiphenylamine + formaldehyde without any condensing agent.	Dark green microcrystalline powder.	7·40; 7·31	Soluble in nitrobenene.
o-Hydroxyphenyldiphenyldiaminotriphenylmethane, $C_{31}H_{36}N_2O$	Diphenylamine + salicylaldehyde with conc. HCl.	Green powder,	6·33; 6·60	Soluble in alkalis, insoluble in most organic solvents.
3:4-Methylenedioxyphenyldiphenyldiaminotriphenylmethane, $C_{33}H_{36}N_2O_2$	Diphenylamine + piperonal in alcoholic solution on water-bath for 12 hrs.	Light green microcrystalline powder.	5·98; 6·16	Soluble in pyridine, nitrobenzene and in conc. sulphuric acid.

TABLE IV.

Comparison of the Dyes derived from Quinoline and Tetrahydroquinoline.

Aldehyde employed.	Shades of dyes derived from quinoline.	Remarks.	Shades of dyes derived from tetrahydroquinoline.	Remarks.
Benzaldehyde.	Light bluish-green.	Auxochromic influence of quinoline feebly developed.	Bluish, green shade deeper than that from quinoline.	Influence of tetrahydroquinoline is evident.
Anisaldehyde.	Orange-yellow.	Green shade of the dye from quinoline is masked.	Light bluish-green.	Green shade is not masked.
Salicylaldehyde.	Light yellow.	Influence of OH is predominant.	Bluish-green.	Influence of OH not evident.
p-Hydroxybenzaldehyde.	Brownish-red.	OH in *para* position having greater influence than in *ortho*.	Bluish ash.	,, ,,
m-Nitrobenzaldehyde.	Yellowish-green.	NO_2 has little auxochromic influence.	Bright green.	
o-, or *p*-Nitrobenzaldehyde.	Light green,	,,		
Dimethyl-*p*-amino-benzaldehyde.	Brown-	NMe_2 producing marked auxochromic effect.	Yellowish-brown.	NMe_2 in *para* position is sufficient to mask the green shade.
β-Resorcylaldehyde.	Orange.	Influence of two OH groups is noteworthy.	Reddish-brown.	Two OH groups change the green shade to reddish-brown.

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Aqueous Solutions of Sodium Aluminate. Part I. Electrical Conductivity.

By Mata Prasad, S. M. Mehta and N. G. Joshi.

No satisfactory proof of the possible number and constitution of sodium aluminates has so far been advanced. Some of these salts have been obtained in a pure state either in the amorphous or crystalline form. The aluminate $Al(ONa)_3$ was prepared by Thomsen and Sauerwein by heating a mixture of cryolite with calcium carbonate and calcium oxide respectively. Goudriaan (*Proc. K. Akad. Wetensch.*, Amsterdam, 1920, **23**, 129; *Rec. trav. chim.*, 1922, **41**, 82) succeeded in isolating the aluminates $4\ Na_2O,\ 3Al_2O_3,\ 16H_2O$ and $4\ Na_2O,\ 3\ Al_2O_3,\ 10H_2O$ in diamond-shaped and needle-like crystals respectively. Allen and Rogers *Amer. Chem. J.*, 1900, **24**, 304) obtained a hard mass of $Na_2Al_2O_4,\ 4H_2O$, by repeatedly digesting a solution of aluminium in sodium hydroxide with alcohol.

But the existence of a large number of sodium aluminates, chiefly meta-aluminate, has been inferred from a study of the properties of solutions of aluminium hydroxide in sodium hydroxide. Since one mole of aluminium hydroxide dissolves in one mole of sodium hydroxide, Prescott (*J. Amer. Chem. Soc.*, 1880, **2**, 27) thought meta-aluminate was present in the solution. The cryoscopic data obtained by Noyes and Whitney (*Z. physikal. Chem.*, 1894, **15**, 694) and by Slade (*Z. Electrochem.*, 1911, **17**, 26) support the above conclusion.

Wood (*J. Chem. Soc.*, 1908, **93**, 417) measured the solubility of aluminium hydroxide in sodium hydroxide and found that his results agreed with the above assumption. But Slade (*Z. Elektrochem.*, 1912, **18**, 1) pointed out that the ratio of Na: Al could be anything from 2:1 to 10:1 depending upon the conditions of precipitation of the aluminium hydroxide.

Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 866) and Blum (*ibid*, 1913, **35**, 1499) measured the changes in the hydrogen-ion concentration, when sodium hydroxide was gradually added to a solution of aluminium chloride. From the breaks in the curve obtained by plotting the volume of NaOH against the hydrogen-ion concentration, they concluded that $NaAlO_2$ was present in solution.

Lyte (*Chem. News*, 1885, **51**, 109) studied the action of aluminium sulphate on dilute and concentrated solutions of sodium aluminate and inferred from the products obtained that the dilute solutions contained $Na_2Al_2O_4$ and the concentrated ones $Na_6Al_2O_6$. Bayer (*Chem. Zeit.*, 1888, **12**, 1209) found that when alumina and soda (1:1) were ignited and the product treated with water, pure Al_2O_3, $3H_2O$ was deposited until the solution contained Al_2O_3 and Na_2O in the ratio of 1 to 6 (moles). But when the ignited mass was placed in as much NaOH solution as was present in the mass, the solution remained clear, thus suggesting that $Na_4Al_2O_5$ and $Na_{12}Al_2O_9$ are really chemical compounds.

Mahin, Ingraham and Stewart (*J. Amer. Chem. Soc.*, 1913, **35**, 30) studied the action of ammonium nitrate on sodium aluminate and found that the ratio of NH_4NO_3/Al_2O_3 was always greater than 2:1. By electrolysing a solution of sodium aluminate, they also found that the ratio of aluminium hydroxide precipitated to the amount of oxygen evolved at the anode was greater than 2:1. Hence they concluded " Colloidal properties of aluminium hydroxide play a far more important part in conditioning its solubility in bases and there is room for doubt as to whether aluminates exist as salts at all." The increased quantity of aluminium hydroxide they obtained was explained as due to the coagulation of the colloidal solution. These conclusions were criticised by Blum (*J. Amer. Chem. Soc.*, 1914, **36**, 2383), who showed that there was no room for doubting the existence of the salt $NaAlO_2$.

Hantzsch (*Z. anorg. Chem.*, 1902, **30**, 297) measured the electrical conductivity of a solution of sodium aluminate with the progress of time and found that the solution first changed into a hydrosol of aluminium hydroxide, then into a gel and finally gave a crystalline precipitate of aluminium hydroxide. Dhar and Chatterjee (*Trans. Faraday Soc.*, 1921, **16**, 122, *addenda*; *Chem. News*, 1920, **121**, 253) found no change in the electrical conductivity of sodium hydroxide on the addition of

small quantities of aluminium hydroxide and hence concluded these to be cases of peptisation and not of chemical combination. On the other hand, Slade and Polack (*Trans. Faraday Soc.*, 1914, **10**, 150) found that although the electrical conductivity of a solution of sodium aluminate showed no change in the first few hours, yet it altered considerably afterwards. They, therefore, concluded that no colloidal alumina was formed and confirmed their conclusions from the ultramicroscopic study of the above solutions.

It appears, therefore, that the exact nature of the solutions of aluminium hydroxide in sodium hydroxide is not correctly known and the results of a systematic study of the various properties of these solutions are wanting. In the present investigation an attempt has been made to measure the electrical conductivity of solutions containing different ratios of Na_2O and Al_2O_3.

Experimental.

Preparation of solutions.—Solutions containing different ratios of Na_2O and Al_2O_3 were prepared by dissolving the requisite quantity of aluminium hydroxide in 2*N* solutions of sodium hydroxide.

Sodium hydroxide solution, free from carbonate, was obtained by preparing a concentrated solution of sodium hydroxide (100 g. in 100 c.c. of water) in a Jena-glass flask, keeping it for 48 hours to allow the carbonate to settle and filtering the supernatant liquid through glass-wool. The strength of the solution was determined by titrating it with a standard acid ; 2*N* solution, used in this investigation, was prepared by diluting this whenever required.

Redistilled water, free from carbon dioxide, was used throughout and the stock solutions were kept in a Jena-glass flasks in an atmosphere free from carbon dioxide.

For the preparation of aluminium hydroxide required for a particular ratio, a weighed amount of aluminium chloride was dissolved in distilled water and the hydroxide precipitated by ammonium hydroxide. The precipitate was washed until free from Cl-ions.

The aluminium hydroxide thus prepared was treated with the calculated quantity of sodium hydroxide solution (2*N*) and the

mixture boiled in a Jena-glass flask till all the aluminium hydroxide was dissolved. The solution was filtered and made up to 250 c.c. In this way the most concentrated solution of any series containing a definite ratio of Na_2O and Al_2O_3 was prepared. The solutions, thus prepared, were allowed to stand for 48 hours before use. The solutions of different strengths were obtained by diluting the stock solution.

The ratio of Na_2O to Al_2O_3 in these solutions was further checked by estimating Na_2O and Al_2O_3 by Lunge's method (*Z. anorg. Chem.* 1890, 227). It was found that solutions containing greater amount of Al_2O_3 than represented by the ratio 1:1 could not be obtained because of the low solubility of aluminium hydroxide in sodium hydroxide.

Burettes, pipettes, measuring flasks, etc. were standardised according to the standard methods.

The electrical conductivity of solutions containing Na_2O and Al_2O_3 in the ratios (*i*) 1:1, (*ii*) 2:1, (*iii*) 3:1, (*iv*) 4:1, (*v*) 3:2 (*vi*) 5:2, was determined at dilutions between 2 *N* and 0·01 *N* at 30° by Kohlrausch's method. As the object of this investigation was not extreme accuracy in the absolute values of the conductivities, the slight change in conductivity, brought about by boiling the solution in Jena-glass flask, has not been taken into consideration.

The resistance box and bridge wire were calibrated by the standard methods. The results obtained are given in the following tables, in which the following symbols have been used:

N = concentration of solutions in term of the normality of sodium hydroxide.

$\triangle$ = equivalent conductivity in r.o.

Several readings were taken for the resistance of a solution and mean of these readings was taken for calculating the specific conductivity (σ); the equivalent conductivity was calculated from the formula

$$\triangle = \frac{\sigma \times 1000}{N}.$$

The equivalent conductivity has been plotted against the concentration and against the ratio of Na_2O and Al_2O_3 and the curves obtained are shown in Figures I and II.

TABLE I.

Ratio $Na_2O : Al_2O_3$	Conc. of Na OH (N).	Equivalent conductivity (△) in r.o.					
		1 :1	2 :1	3 :1	4 :1	3 :2	5 :2
	2·00	58·75	97·50	67·70	123·80	73·20	83·00
	1·00	70·65	112·80	82·20	153·60	90·03	101·90
	0·666	76·78	126·10	93·11	167·00	107·80	109·20
	0·500	81·26	130·50	99·24	177·06	117·96	122·20
	0·400	81·00	138·60	103·70	181·80	119·60	129·50
	0·333	—	143·60	117·40	187·90	134·30	135·80
	0·285	102·30	145·20	131·20	188·50	140·30	141·90
	0·250	105·36	148·48	137·60	191·00	141·60	147·28
	0·220	109·40	—	142·80	195·30	—	155·10
	0·200	111·50	154·00	152·00	195·35	149·50	158·50
	0·100	113·00	161·20	185·00	—	157·00	168·80
	0·050	118·90	168·80	203·20	—	166·20	175·90
	0·010	122·00	184·00	222·00	—	181·00	198·00

Discussion.

It will be seen from Table I, that the equivalent conductivity of sodium hydroxide is considerably decreased by the addition of aluminium hydroxide. These observations are not in agreement with those of Dhar and Chatterjee (*loc. cit.*). The results described above agree very nearly with those calculated by extrapolating the conductivity-time curves obtained by Slade and Polack (*loc. cit.*).

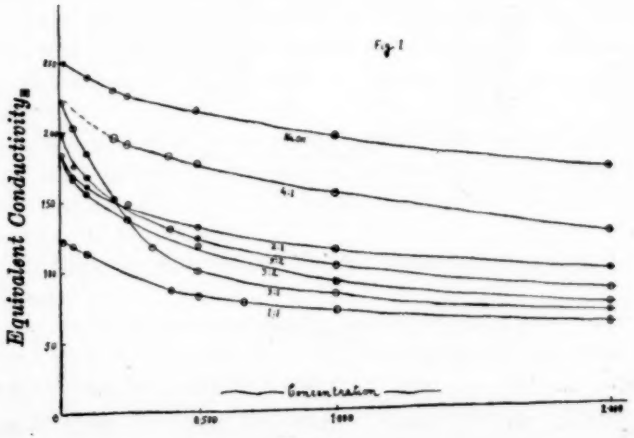

FIG. 1.

From Fig. 1, it will be seen that the equivalent conductivity of solutions, containing different ratios of Na_2O and Al_2O_3 increases with dilution. The increase in the conductivity is much greater in dilute solutions than in the concentrated ones. The solution containing the ratio 3 : 1 shows very rapid changes below 0·50 *N*. The increase in the conductivity of these solutions on dilution is due to an increased concentration of mobile hydroxyl ion, probably caused by the greater degree of hydrolysis of the salts present in the solutions.

The value of the equivalent conductivity at infinite dilution of the solutions containing different ratios of Na_2O and Al_2O_3 has been determined by the method adopted by Harman (*J. Phys. Chem.*, 1925, **29**, 1155) for the purpose. The equivalent conductivity is plotted against the logarithm of normality and the following values have been obtained for the equivalent conductivity at infinite dilution by extrapolating the curves shown in Fig. 2.

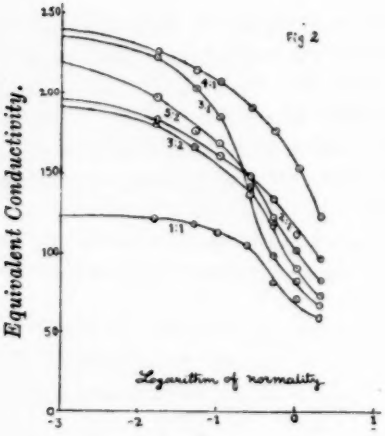

FIG. 2.

TABLE II.

Ratio ...	1 :1	3 :2	2 :1	5 :2	3 :1	4 :1
Δ_∞ ...	123	192	196	220	236	240

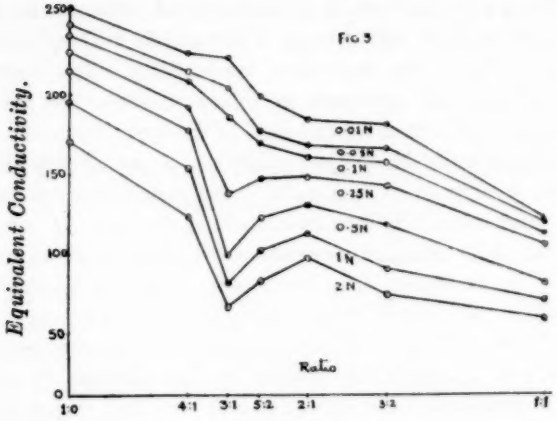

FIG. 3.

Very interesting conclusions are obtained from Fig. 3, in which the equivalent conductivity has been plotted against the ratio. In the case of the dilute solutions, it will be seen that

(1) the equivalent conductivity of sodium hydroxide solution to which alumina is added falls rapidly but not linearly until the ratio 2:1 is reached;

(2) the equivalent conductivities corresponding to ratios 2:1 and 3:2 are almost equal, which is rather remarkable ;

(3) the equivalent conductivity falls rapidly as the ratio is changed from 3:2 to 1:1.

There are no sharp changes in the curves at low dilutions (below 0·25 *N*) and hence no inference regarding the existence of any aluminates in solution can be drawn from a study of these curves.

In the case of the concentrated solutions, it is noticed that

(1) the equivalent conductivity of sodium hydroxide solution to which alumina is added falls rather rapidly until the ratio 3:1 is reached ;

(2) there is a sharp change in the curve corresponding to the ratio 3:1 ;

(3) the equivalent conductivity, at and above 0·25 *N*, increases as the ratio is increased from 3:1 to 5:2 and 2:1 and then falls, as the ratio is changed to 3:2 and 1:1.

The sharp change at the ratio 3:1 would seem to indicate the formation of the salt $Na_6Al_2O_6$ in solution. This salt is probably

hydrolysed to a very small extent in concentrated solutions and hence there is such marked suppression of the mobile hydroxyl ions and the consequent fall in the equivalent conductivity. The degree of hydrolysis of the salt increases in dilute solutions and hence no marked change of direction is noticeable in the upper three curves.

The increase in conductivity of solutions of ratios 5:2 and 2:1 may appear abnormal at first sight. But considering the relative increase in the sodium hydroxide content as the ratio is increased from 1:1 to 3:2 and 2:1, the observed increase in the equivalent conductivity is expected. The formation of the salt $Na_6Al_2O_6$ in solution which, as stated above, probably, hydrolyses to a very small extent in concentrated solutions, produces a considerable fall in the OH-ion concentration, inspite of the increase of sodium hydroxide in solutions of the ratios 5:2 and 3:1 and hence there is a fall in the equivalent conductivity in solutions of these ratios.

As solutions containing aluminium hydroxide, dissolved in sodium hydroxide in ratios greater than 1:1, could not be obtained because of the limited solubility of the former in the latter, no information could be obtained from these experiments regarding the existence of the well known salt $Na_2Al_2O_4$.

The hydrogen-ion concentrations of these solutions are also being measured and in view of these measurements, the points raised here will be further discussed in a subsequent paper.

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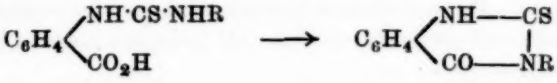
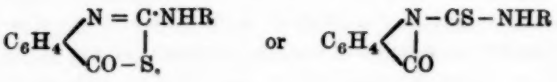
Ring-Closure of *o*-Thiocarbamidobenzoic Acids: Studies in Isomerism.

By Tejendra Nath Ghosh.

When anthranilic acid and phenyl mustard oil are allowed to react in the cold, *o*-phenylthiocarbamidobenzoic acid (I, R=Ph) and 4-keto-2-thio-3-phenyl-1:2:3:4-tetrahydroquinazoline (II, R=Ph) are obtained (McCoy, *J. Amer. Chem. Soc.*, 1899, **21**, 147). Anthranilic acid has now been condensed with various mustard oils in hot alcoholic solution and in each case only the corresponding quinazoline has been obtained. This shows that the arylthiocarbamidobenzoic acid which is first formed very easily passes into the quinazoline with loss of a molecule of water.



(I) (II)



(III) (IV)

(where R=phenyl, *p*-tolyl, *o*-tolyl, 1:3:4-xylyl, and allyl).

A remarkable transformation takes place when compound (II, R=Ph or *p*-tolyl) is heated with strong sulphuric acid at 125-130°. The products of the reaction are isomeric with the original substances but possess different properties.

In fact, the compound (II) is acidic in nature and gives a disulphide, whereas its transformation product (III) is insoluble in alkali but soluble in acids. The alternative formula (IV) is rejected on the ground that the compound actually isolated is not desulphurised by yellow oxide of mercury. As no intermediate product has been isolated, it is difficult to suggest, at present, the real mechanism of the above reaction.

The action of concentrated sulphuric acid upon *o*-phenylthiocarbamidobenzoic acid also leads to the compound (III, R=Ph).

The behaviour of 4-keto-2-thio-3-allyl-1 : 2 : 3 : 4-tetrahydroquinazoline appears to be different from that observed with the other quinazolines, in so far as it gets decomposed on boiling with strong sulphuric acid giving rise to a sulphur-free crystalline compound (m. p. 207°). The yield of this compound is so poor that further studies could not be made. When, however, the compound (II, R=allyl) is boiled with strong hydrochloric acid, 2-allylamino-6-keto-4 : 5-benzo-1 : 3-thiazine (III, R=allyl) is obtained.

Experimental.

4-Keto-2-thio-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline (II, R=Ph).—An alcoholic solution of anthranilic acid (5 g.) was heated under reflux on the water-bath with phenyl mustard oil (5 g.) for about an hour when a crystalline precipitate was obtained, which crystallised from acetic acid in colourless plates, m. p. above 300° (yield 7 g.). (Found: N, 11·19. $C_{14}H_{10}ON_2S$ requires N, 11·02 per cent.). It is soluble in cold dilute alkali, and insoluble in sodium carbonate or bicarbonate solutions. It gives an insoluble lead salt with lead acetate.

Disulphide.—Iodine solution (in potassium iodide) was added drop by drop to an acetic acid solution of the above compound (II) and gently warmed. On dilution with water it gave a yellowish amorphous mass which was washed free from excess of iodine with potassium iodide solution, water and finally with alcohol; m. p. 250-252°. (Found: N, 11·31. $C_{28}H_{18}O_2N_4S_2$ requires N, 11·06 per cent.).

4-Keto-2-thio-3-p-tolyl-1 : 2 : 3 : 4-tetrahydroquinazoline (II, R=p-*tolyl*).—The method of preparation was the same as in the case of the preceding compound. It was crystallised from acetic acid in colourless plates, m. p. 310°. (Found: N, 10·42. $C_{15}H_{12}ON_2S$ requires N, 10·44 per cent.).

4-Keto-2-thio-3-o-tolyl-1 : 2 : 3 : 4-tetrahydroquinazoline (II, R=o-*tolyl*).—Obtained in a similar manner it crystallised from acetic acid in colourless plates, m. p. 268-270°. (Found: N, 10·04. $C_{15}H_{12}ON_2S$ requires N, 10·44 per cent.).

The *disulphide* was prepared in the usual manner; m. p. 215° (shrinking at 200°). (Found: N, 10·12. $C_{30}H_{22}O_2N_4S_2$ requires N, 10·48 per cent.).

4-*Keto*-2-*thio*-3-(1′:3′:4′)-*xylyl*-1:2:3: 4-*tetrahydroquinazoline* (II, R=*xylyl*).—It was crystallised from acetic acid in colourless plates, m. p. 259-260°. (Found: N, 9·54. $C_{16}H_{14}ON_2S$ requires N, 9·93 per cent.).

4-*Keto*-2-*thio*-3-*allyl*-1: 2: 3: 4-*tetrahydroquinazoline*.—It was crystallised from alcohol in colourless plates, m. p. 206-207°. (Found: N, 13·25. $C_{11}H_{10}ON_2S$ requires N, 12·84 per cent.). It is soluble in dilute caustic soda and insoluble in sodium carbonate or bicarbonate solutions.

2-*Anilino*-3-*keto*-4: 5-*benzo*-1: 3-*thiazine* (III, R=Ph).—(*a*) 4-Keto-2-thio-3-phenyl-1: 2: 3: 4-tetrahydroquinazoline (5 g.) was heated with strong sulphuric acid (30 c.c.) in an oil-bath at 125-130° for 3—4 hours. The clear solution, thus obtained, was cooled and diluted with cold water when a precipitate came out which further crystallised from alcohol in fine colourless needles, m. p. 184-185°. (yield, 3·5 g.). It is insoluble in both cold and hot alkali. (Found: N, 11·27; S, 13·01. $C_{14}H_{10}ON_2S$ requires N, 11·02; S, 12·59 per cent.).

(*b*) *o*-Phenylthiocarbamidobenzoic acid (4 g., prepared according to the method of McCoy, *loc. cit.*) was heated with strong sulphuric acid (30 c.c.) in an oil-bath at 125-130° for about 3 hours. The clear solution, on dilution with ice-cold water, gave a precipitate which crystallised from alcohol in colourless needles, m. p. 184-185°. (yield, 1·5 g.). It is insoluble in both cold and hot alkali. (Found: N, 11·31. $C_{14}H_{10}ON_2S$ requires N, 11·02 per cent.). The identity of this compound with that prepared by the above method was further confirmed by determining a mixed melting point.

2-p-*Tolylamino*-6-*keto*-4: 5-*benzo*-1: 3-*thiazine* (III, R=p-*tolyl*). .—The method of prepartion was the same as in the case of the preceding compound. It was crystallised from alcohol in colourless needles, m. p. 235°. It is insoluble in cold or hot alkali. (Found: N, 10·48. $C_{15}H_{12}ON_2S$ requires N, 10·44 per cent.).

2-*Allylamino*-6-*keto*-4: 5-*benzo*-1: 3-*thiazine* (III, R=*allyl*).—4-Keto-2-thio-3-allyl-1: 2: 3: 4-tetrahydroquinazoline (5 g.) was boiled with hydrochloric acid (50 c. c., *d* 1·19) for about 3 hours. The clear solution was allowed to cool when shining colourless needles came out which crystallised from hot water; m. p. 231-232°. It is the hydrochloride of a base and soluble in warm water from which the free base was obtained by the addition of dilute caustic potash solution. The base crystallised from hot water in shining colourless needles; m. p. 115° (yield, 3 g.) It is insoluble in cold

water and in cold dilute alkali. (Found: N, 13·15; S, 14·25. $C_{11}H_{10}ON_2S$ requires N, 12·84; S, 14·67 per cent.).

Further work in this line is in progress.

My best thanks are due to Professor P. C. Guha, D.Sc., for the kind interest he has taken in this investigation.

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The Photochemical Decomposition of Nitrous Acid.

By K. S. Murty and N. R. Dhar.

Mukerji and Dhar (*Z. Electrochem.*, 1925, **31**, 255) have shown that the decomposition of nitrous acid is markedly accelerated by light, and that the velocity coefficient both in light and in the dark increases slowly with the concentration of nitrous acid. The velocity coefficients are considerably greater (200-400 per cent.) when open vessels are employed instead of closed ones. This is ascribed to the escape of nitric oxide from open vessels. Mukerji and Dhar (*loc. cit.*) have shown that the acceleration caused by light is more marked with closed than with open vessels.

In this communication, further results on the kinetics, temperature coefficients, quantum efficiency and the influence of the intensity of different wave-lengths are given.

The general experimental arrangement is the same as that described in a previous paper (Bhattacharya and Dhar, *J. Indian Chem. Soc.*, 1929, **6**, 143). A cubical quartz cell with plane parallel sides (4 cm.) served as the reaction vessel. Nitrous acid was prepared by the method described in a previous paper (Mukerji and Dhar, *loc. cit.*). The progress of the reaction was followed by determining the quantity of unchanged nitrous acid from time to time by the permanganate method.

Kinetics and Temperature Coefficients.

To obtain the regions of mean wave-lengths 4725Å and 7304Å respectively, a combination of two gelatine films, " Wallace M and S " filters, were used.

The experimental results are as follows.

Table I.

Dark.

Temperature ...	20°	30°	40°	50°
k_1 (monomolecular) ...	0·001882	0·002973	0·006552	0·012880
Temp. coefficient ...		1·58	2·21	1·95

TABLE II.

Region.	Temp.	k_1 (monomolecular).	k_1 (monomolecular after deducting dark reaction).	Temp. coeff. (without deducting the dark reaction).	Temp. coeff. (after deducting dark reaction).
Sunlight	30°	0·007505	0·004532		
Total light from a 1000-watt gas-filled tungsten filament lamp.	20°	0·003606	0·001724		
	30°	0·005593	0·002620	1·55	1·52
	40°	0·008376	0·001824	1·50	0·69
	50°	0·013290	0·000410	1·51	0·22
(5000-4450)Å. Mean 4725Å.	20°	0·003370	0·001488		
	30°	0·005259	0·002279	1·56	1·53
	40°	0·008130	0.001578	1·55	0·69
(5850-5450)Å. Mean 5650Å.	20°	0·002953	0·001071		
	30°	0·004606	0·001633	1·56	1·53
	40°	0·007674	0·001122	1·66	0·69
Mean 7304Å.	20°	0·002695	0·000813		
	30°	0·004194	0·001221	1·56	1·50
	40°	0·007392	0·00840	1·77	0·69
8500Å *	30°	0·003799	0·000826		

Determination of Quantum Yield.

The energy absorbed by the reactant was measured with a sensetive galvanometer (Hartmann-Braun) and a Moll-thermopile. The deflections of the galvanometer as read on the scale were calibrated by a Hefner-lamp (*cf.* Gehrlach, *Physikal Z.*, 1913, **14**, 577).

The results are summarised in the following table.

TABLE III.

	Quantum yield for wave lengths (Å)			
Temp.	4725	5650	7304	8500
20°	10	9	4	—
30°	15	11	7	5
40°	8	7·8	1·2	—

* Blue cobalt glass cell filled with saturated potasium dichromate solution.

The influence of the variation of the intensity of incident light on the velocity of the photochemical decomposition of nitrous acid.

A screened Iris-diaphragm was placed between the source of light and the reaction vessel so as to avoid extraneous light from falling on the reacting system. The intensity of light was taken to be directly proportional to the area of aperture. In each case the extent of the reaction that would have taken place in dark was deducted from the total change observed in light, in order to obtain the change due to light alone.

TABLE IV.*

Temp. = 30° k_1 (dark) = 0·002973

Diameter of aperture (cm.).	A 1000-watt lamp.		B 4725Å.		C 5650Å.		
	k_1	k_1^1	k_1	k_1^1	k_1	k_1^1,	
2	0·005393	0·002420	0·005179	0·00221	0·004592	0·00162	I
0·8	0·004544	0·001570	0·004505	0·00153	0·004035	0·00106	II
0·4	0·003969	0·001000	0·003876	0·00090	0·003536	0·00058	III

TABLE V.

	Ratio of velocities.		If proportional to $\sqrt{I}$	If proportional to $\sqrt[3]{I}$
A.	$\frac{I}{II} = \frac{0·00242}{0·00157}$	= 1·5	2·5	1·8
	$\frac{II}{III} = \frac{0·00157}{0·00100}$	= 1·6	2·0	1·6
	$\frac{I}{III} = \frac{0·00242}{0·00100}$	= 2·4	5·0	2·9
B.	$\frac{I}{II} = \frac{0·00221}{0·00153}$	= 1·5	2·5	1·8
	$\frac{II}{III} = \frac{0·00153}{0·00090}$	= 1·7	2·0	1·6
	$\frac{I}{III} = \frac{0·00221}{0·00090}$	= 2·5	5·0	2·9
C.	$\frac{I}{II} = \frac{0·00162}{0·00106}$	= 1·5	2·5	1·8
	$\frac{II}{III} = \frac{0·00106}{0·00058}$	= 1·8	2·0	1·6
	$\frac{I}{III} = \frac{0·00162}{0·000580}$	= 2·8	5·0	2·9

* In the above table k_1, k_1' are the monomolecular constants calculated respectively from the observed data and for that corrected for the reaction in the dark.

It will thus be seen that the velocity of the photo-decomposition of nitrous acid is proportional to the cube root of the intensity of the incident light.

Discussion of Results.

An examination of Table I shows that the temperature coefficient of the thermal reaction increases from 1·58 (between 20° and 30°) to 2·21 (between 30° and 40°); between 40° and 50° there is a slight fall in the temperature coefficient, the value being 1·96. Similar increase in the temperature coefficient with elevation of temperature was noticed for this reaction by Ray, Dey and Ghosh (*J. Chem. Soc.*, 1917, **111**, 413) and Mukerji and Dhar (*loc. cit.*). The latter workers obtained the following values:—

$$\frac{k_{20}^{\circ}}{k_{10}^{\circ}} = 1{\cdot}1, \quad \frac{k_{30}^{\circ}}{k_{20}^{\circ}} = 1{\cdot}5, \quad \frac{k_{40}^{\circ}}{k_{30}^{\circ}} = 1{\cdot}9.$$

At first sight, this increase in the temperature coefficient with elevation of temperature would seem anomalous, as the temperature coefficient of most thermal reactions falls with temperature. But this can be explained as follows:—The decomposition of nitrous acid is a reversible reaction,

$$3\,HNO_2 \rightleftharpoons HNO_3 + 2\,NO + H_2O.$$

Any factor facilitating the escape of nitric oxide will produce an increase in the rate of decomposition of nitrous acid. The solubility of nitric oxide diminishes with the temperature. Two factors thus contribute to the increase of velocity; one, the usual factor tending to increase the reaction velocity with the temperature; the other, the increasing facility for the escape of nitric oxide at higher temperature. Thus an abnormal increase in velocity with increasing temperature would be observed, and this results in the increase of temperature coefficient with the elevation of temperature.

It has been stated before that the temperature coefficients of the purely photochemical reaction in the various regions fall below unity in the temperature range 30° to 40° (*vide* Table II).

This is the reverse of the effect observed with most photochemical reactions. This may be due to either one or both of the two following factors. Firstly, there may be a decrease in absorption of light by the reacting system in passing from 30° to 40°; and

secondly the reverse reaction, the reduction of nitric acid by nitric oxide to nitrous acid ($HNO_3 + H_2O + 2NO \rightleftharpoons 3HNO_2$) may be photochemical in nature and may be proceeding at a considerably greater speed at 40° than at 30°. Both factors seem to be at work in the case under consideration.

The results of absorption measurements tabulated below show a slight fall in the absorption.

Temperature.	Absorption corresponding to cm. on the scale.			
	Total light	4725Å	5650Å	7304Å
30°	26·56	6·98	5·18	6·49
40°	23·82	6·25	4·5	5·75

That the reverse reaction is also taking place photochemically with a greater speed at 40° than at 30° will be evident from the following considerations. If some of the absorbed light energy is utilised in the reverse reaction, then there should be an apparent reduction in the quantum yield for the direct reaction is passing from 30° to 40°. Experiments show that such is the case. To give an example, the quantum yield for the wave-length 7304Å is .7 at 30°, whereas at 40°, it is 1 ·2. The values of the quantum yield have been calculated on the assumption that the whole of the absorbed light energy is utilised in the direct reaction.

Only a few instances are on record where the temperature coefficients of a photochemical reaction are less than unity (Chapman and Gee, *J. Chem. Soc.*, 1911, **99**, 1726 ; Trautz, *Z. Elektrochem.*, 1915, **21**, 336). Trautz (*loc. cit.*) worked at 18° and 98°. An increase in temperature of 80°, decreases the velocity of formation of sulphuryl chloride corresponding to a temperature coefficient of 0·88 per 10°. The explanation given above appears to be applicable to these cases also, because these reactions are also reversible.

Einstein's law of photochemical equivalence does not hold good for this photochemical reaction, which is exothermal in nature. Dhar (*Trans. Faraday Soc.*, 1925, **21**, 489) has emphasised that the law of photochemical equivalence usually fails in exothermal photochemical reactions.

Summary.

1. The decomposition of nitrous acid is markedly accelerated by light. The kinetics, temperature coefficients and energetics of this photochemical reaction have been studied in radiations of wave-lengths 4725Å, 5650Å, 7304Å and 8500Å.

2. The temperature coefficient of the thermal reaction increase from 1·58 between 20° to 30° to 2·21 between 30° to 40°. An explanation has been given for this anomalous increase of temperature coefficient with elevation of temperature.

3. The temperature coefficients of the purely photochemical reaction fall below unity in the temperature range 30° to 40° and 40° to 50°. A suitable explanation has been offered for this peculiarity.

4. The influence of varying the intensity of incident radiation on the velocity of this reaction has been studied. The monomolecular velocity coefficient has been found to be proportional to the cube root of the intensity.

5. This reaction does not follow Einstein's law of photochemical equivalence.

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The Function of Br_3^- and I_3^- Ions and the Influence of Cl^- Ions in some Oxidation Reactions in Light.

By R. M. Purkayastha.

The interaction between organic acids and bromine in light and in darkness have recently been investigated (Ghosh and Mukherjee, *J. Indian Chem. Soc.*, 1925, **2**, 165; Ghosh and Basu, *ibid*, 1928, **5**, 343,; Purkayastha, *ibid*, 1929, **6**, 376, 385; Ghosh and Purkayastha, *Z. Phys. Chem.*, 1930, B7, 276, 285). In absence of a bromide and with an excess of mandelic or phenyllactic acid the reactions were bimolecular in the dark and unimolecular in light (Purkayastha, *loc. cit.*). When a bromide was present in excess, the dark and light reactions were unimolecular and zeromolecular respectively. The velocity constants in both cases diminished with the concentration of the bromide. It was suggested that in light the active bromine atoms and in the dark the activated bromine molecules were responsible for starting the chain of reactions (Ghosh and Purkayastha, *loc. cit.*).

In absence of a bromide the velocity for the dark reaction is given by

$$-d\frac{[Br_2]}{dt} = \frac{k'[Br_2 \text{ free}]^2\ [A']}{k''[Br_2 \text{ initial}]^2 + 1} \quad \ldots (1)$$

When the bromide, a powerful inhibitor, is present in excess the chain length is considerably shortened and the velocity is given by

$$-d\frac{[Br_2]}{dt} = k[Br_2 \text{ total}]\,[A']\left[\frac{k_1}{Br} + 1\right] \quad \ldots (2)$$

For the light reactions in absence and in presence of an excess of bromide we get respectively,

$$\frac{-d[Br_2]}{dt} = \sqrt{kI}\ [A']\ \frac{k_a[Br_2]}{k_b[Br_2 \text{ initial}]^2 + k_c} \quad \ldots (3)$$

and $$\frac{-d[Br_2]}{dt} = \sqrt{kI}[A']\left[\frac{k_1}{Br} + 1\right] \quad \ldots (4)$$

where [A′] is the concentration of the anion of the reacting organic acid and [Br′] concentration of bromine ion.

With an excess of reacting acid equation (4) shows that the reaction becomes zeromolecular.

Zeromolecular constants should also be obtained for radiations which can effect the decomposition of bromine molecules into atoms. This has been experimentally realised. Quite good zeromolecular constants were obtained for the wave-lengths (given in microns) 542, 488, 448, 408, and 365. Some of the results are given below.

TABLE I.

Wave-length = 542$\mu\mu$. Temp. = 30°.
·31 *M*-Mandelic acid; ·127 *M*-KBr; ·0155 *M*-Br_2.

Time in minutes ...	0	45	90	140	205
$(a-x)$ ...	12·5	11·6	10·75	9·5	8·1
x/t ...		·020	·019	·021	·021

TABLE II.

Wave-length = 366$\mu\mu$. Temp. = 30°.
·38 *M*-Lactic acid; ·192 *M*-KBr; ·0226 *M*-Br_2.

Time in minutes ...	0	30	60	90	120
$(a-x)$ ...	19·05	18·15	17·25	16·3	15·35
x/t ...		·030	·030	·0316	·0316

TABLE III.

Wave-length = 448$\mu\mu$. ·34*M*-Lactic acid. Temp. = 30°.

KBr Conc.	Br. Conc.	Total Br_2 conc. in μ. mol.	x/t.	$x/t \Big/ \frac{h_1}{Br} + 1.$
·2	·15	·03	·0383	31×10^{-4}
·133	·1033	·0187	·054	31 × ,,
·0833	·067	·0117	·083	31 × ,,
·1	·08	·015	·064	29 × ,,
·0833	·067	·0071	·082	31 × ,,
·125	·0973	·0107	·058	31 × ,,
·167	·127	·0144	·045	31 × ,,
·075	·062	·0107	·078	28 × ,,
·208	·156	·0189	·034	29 × ,,

Similar results were also obtained with mandelic acid.

TABLE IV.

Influence of Thickness of Reaction Layer.

·192 *M*-KBr; ·0241*M*-Br_2; Temp. = 30°.

Acid conc.	Mean wave-length ($\mu\mu$).	Inverse ratio of the thickness of reaction layers.	Ratio of velocity constants.
·31*M*	390	2	1·7
(Mandelic acid)	408	2	1·54
	488	2	1·16
·33*M*	390	2	1·65
(Lactic acid)	408	2	1·54
	488	2	1·15

The reaction cells were ·5 cm. and 1 cm. thick respectively. For complete absorption of light the velocity constants should vary as the inverse ratio of the thickness of the reaction layers. The above results show that at 488$\mu\mu$ the ratio of the velocity constants is only 1·15 or the light absorption is far from complete whereas at 390$\mu\mu$ the ratio is 1·7 and the absorption is very strong.

Influence of Cl^-*ions on the Photochemical Oxidation by Bromine.*

The oxidation of several hydroxy acids by bromine was shown to be strongly accelerated by the presence of chlorine ions The accelaration was observed to be nearly proportional to the concentration of chlorine ions. Ghosh and Purkayastha (*loc. cit.*) attributed it to the activation of bromine molecules by collision with chlorine ions.

The results given in Table V show that instead of an acceleration, the light reactions are appreciably retarded by the presence of chlorine ions. The energy of activation of a bromine molecule is no doubt less than that for its dissociation into atoms and while bromine molecules may become activated by collision with chlorine ions, the active bromine atoms may suffer deactivation on collision with them. It has also been found that the retardation increases with the concentration of chlorine ions.

In all cases however where a bromide is present, the dark reactions are unimolecular but the light reactions are zeromolecular.

The reaction between phenyllactic acid and bromine gives nearly unimolecular constants on account of the fact that the dark reaction

is considerable. Thus in presence of ·222*M*-KCl the unimolecular constant for the thermal reaction is ·0033 and for the photochemical reaction, ·00484. The last column in Table V contains the velocity constants due to light only.

TABLE V.

Blue light. Temp. = 26°.

·0522*M*-Br ; ·0116*M*-HBr ; ·0844*M*-Br_2.

Acid conc.	KCl Conc.	k_0(zeromolecular).
·278*M* (Mandelic)	0	·094
	·0555	·091
	·222	·087
·278*M* (Lactic)	0	·087
	·222	·080
		k (unimolecular).
·0833*M* (Phenyllactic)	0	·00187
	·0555	·00171
	·222	·00154

The Function of I_3^- ions in Photochemical Oxidation by Iodine.

Since iodine forms I_3 ions in presence of a soluble iodide a similar mechanism of the oxidation by iodine may be expected. Oxidation of sodium salts of organic acids by iodine in presence of potassium iodide has been studied by Dhar and others (*J. Phys Chem.*, 1928, **32**, 1308 ; *J. Indian Chem. Soc.*, 1929, **6**, 451, 473). The reactions were found to be either unimolecular or semimolecular. It appears from their data that unimolecular constants are obtained in those instances in which the light reaction proceeds very slowly (about 5 to 10%) in comparison to that in the dark, for instance, sodium lactate and iodine, sodium tartrate and iodine; whereas semimolecular constants are obtained in the reactions between sodium citrate, sodium formate, sodium malate and iodine in which the rate of the dark reaction is quite comparable to that of the light reaction. It should be noted that the dark reactions are in all cases unimolecular. It is evident that in the first group, even if the light reaction be of a different order, the combined light and thermal reaction will very nearly conform to the order of the dark reaction but in the second group the observed order of the reaction will be

intermediate between the orders of the light and dark reactions, on the assumption that the light reaction is zeromolecular and a semimolecular constant is naturally expected. Dhar and Mukerji (*J. Phys. Chem.*, *loc. cit.*) give the following values for the combined light and thermal effects for the reaction between sodium formate and iodine. The first three columns in Table VI and VII contain their results.

TABLE VI.

White light. Temp. = 30°.

·156*N*-Sodium formate ; ·0084*N*-Iodine ; ·031*N*-Potassium iodide ; ·137*N*-Sodium acetate.

Time in minutes.	Combined light and thermal reaction $[a-(x_1+x_2)]$.	$k_{\frac{1}{2}}$ (Semi-molecular).	k_1 Amount of change due to dark reaction in each successive interval as calculated from unimolecular const. $k_1 = ·01$.	k_2 Amount of change due to light reaction in each successive interval.	k_0 (Zero-molecular).
0	3·65	—	—	—	—
9	2·8	·0528	·65	·2	·022
15·5	2·24	·053	·39	·17	·026
24·5	1·5	·0557	·44	·3	[·033]
30	1·2	·0544	·18	·12	·022
38	·8	·0533	·2	·2	·025

TABLE VII. (Higher intensity).

0	3·65	—	—	—	—
8	2·8	·0600	·61	·24	·030
15	2·1	·0611	·42	·28	·040
22	1·55	·0605	·32	·24	·034
30	1	·0607	·26	·29	·036

Dhar (*J. Chem. Soc.*, 1917, **111**, 731) finds the velocity constant k_1 for the dark reaction to be ·00556 at 25° and 3·89 as the temperture coefficient. The concentrations of sodium formate, iodine and potassium iodide were ·1667*N*, ·0088*N*, and ·034*N* respectively. The concentrations of the reacting substances are nearly the same in

both cases. The velocity constant for the dark reaction will be nearly ·01 at 30°. The amount of change in successive intervals due to the thermal reaction has been calculated from the expression $k^1 = \frac{1}{t} \log \frac{a}{(a-x)}$ with this value of k_1. Appreciable variation in the value of k_1 will not materially alter the nature of the results. It will of course affect the absolute values obtained. The results given in Tables VI and VII make it clear that the light reactions are truly zeromolecular. The semimolecular constants obtained by Dhar is to be attributed to the combined light and thermal effects.

The author wishes to express his sincere thanks to Prof. J. C. Ghosh for his kind interest and suggestions.

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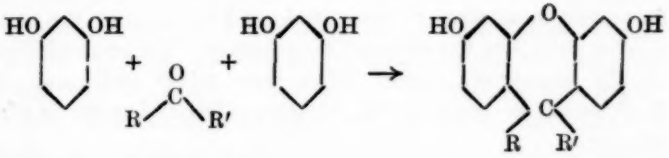
Condensation of Ketones with Resorcinol. Part II.

By Rajendra Nath Sen, Nalin Chandra Chattopadhya and Suresh Chandra Sen-Gupta.

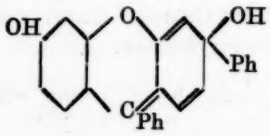
The condensation of one molecule of ketone with one molecule of resorcinol has been described in Part I (*J. Indian Chem. Soc.*, 1930, **7**, 167). In the present investigation various ketones have been condensed with two molecules of resorcinol in presence of anhydrous zinc chloride and hydrochloric acid gas, the reaction taking place in the following manner.



A similar type of condensation was effected previously between benzil and four molecules of resorcinol by Liebig (*Ber.*, 1899, **32**, 2332) and between anthraquinone and resorcinol (2 mols.) by Scharwin and Kusnezof (*Ber.*, 1903, **36**, 2020) in presence of stannic chloride.

The most striking fact about the various condensation products described in this paper is that though they do not admit of quinonoid configuration according to the ordinary modes of tautomerisation, yet they are all coloured compounds producing more or less deeply coloured solutions with caustic alkali and also possessing dyeing properties in varying degrees. Thus they form an interesting group of non-quinonoid dyes, producing yellow, orange and brown shades on wool and silk, the brominated products producing beautiful red and bluish-red shades. Instances of non-quinonoid compounds (such as benzalnitroanilines, acenaphthylene, azobenzene, etc.) possessing colour, though rare, are not altogether unknown; but under no circumstances can they be regarded as true dyes.

By an extraordinary manipulation some sort of partially quinonoid structure may be given to some of the condensation products described in this paper after the analogy of the structure attributed to triphenylmethyl by Jacobson and others. Thus the anhydride of tetrahydroxytetraphenylmethane may be represented as having the following half-quinonoid structure,



but such an arrangement is altogether excluded in the case of the condensation products from fluorenone, camphor, *cyclo*hexanone and antipyrine.

The condensation products with resorcinol are all more or less fluorescent in alkaline, alcoholic, and pyridine solutions, the alcoholic solution exhibiting the strongest fluorescence. The bromo-derivatives of the compounds possess much deep colour (red) and exhibit fluorescence in alcoholic and acetone solutions but not in alkaline solution.

The different condensation products obtained also afford an interesting study of the relation between colour and constitution. 4:4'-Dihydroxytetraphenylmethane (*J. Chem. Soc.*, 1901, **79**, 1209) has been described as colourless, but the condensation product (I, R,R'=Ph) of benzophenone with resorcinol containing a pyrone ring in addition, possesses a dark brown colour, dissolves in alkali with deep orange colour and dyes wool and silk beautiful brownish-yellow shades. The replacement of one or two of the phenyl groups by methyl much weakens the tinctorial character as is shown by the condensation products derived from acetophenone and acetone, which dissolve in alkali solution with lighter colour and possess much feebler dyeing properties, the latter having very slight affinity for wool or silk.

The fluorescence of the three compounds however in alkaline or alcoholic solutions does not appreciably differ. But it is interesting to note that like the tinctorial character, the yields of the three compounds also vary with the number of the benzene nuclei, that of the benzophenone compound being greatest. It therefore appears that the reactivity of the CO-group under the conditions of the

present investigation increases with the increase in the negative character of the radicles in the ketone. It is also interesting to note that fluorenone reacts more rapidly than benzophenone, giving a better yield.

In the case of the condensation products of diketones like phenanthraquinone and benzil with resorcinol two series of compounds have been obtained, (*a*) the reaction taking place between one carbonyl group and two molecules of resorcinol, and (*b*) between two carbonyl groups and four molecules of resorcinol. It is interesting to note that the compounds of the second series exhibit much deeper colour and also stronger fluorescence, probably on account of their symmetrical structure.

Experimental.

General Method.—A mixture of the ketone (1 mol.) and resorcinol (2 mols.) was heated in a flask until they melted ; powdered anhydrous zinc chloride was then added and dry hydrochloric acid gas was passed into the flask. The temperature was gradually raised to 180-190° and heating continued for 3-5 hours. The product was thoroughly washed with dilute hydrochloric acid, dissovled in dilute sodium hydroxide solution, filtered, and precipitated by dilute acetic or hydrochloric acid. The alkali-acid treatment was repeated several times. Finally it was crystallised from some organic solvent.

Condensation with Open-chain Monoketones.

Anhydride of Tetrahydroxytetraphenylmethane (I, R′=Ph) was prepared by heating benzophenone (3·6 g.) with resorcinol (4·4 g.) for 4—5 hours at 180°−190°. The crude product was washed successively with benzene, chloroform and ether and then dissolved in warm alcohol or acetone from which it separated as a brown microcrystalline powder melting at 125-127° (yield. 70%). It shows orange-green fluorescence in alkali and dyes wool and silk brownish-yellow. (Found: C, 81·8 ; H, 4·7. $C_{25}H_{18}O_3$ requires C, 81·9; H, 4·9 per cent.).

Dipotassium Salt.—(Found: K, 17·8. $C_{25}H_{18}O_3$ requires K, 17·6 per cent.).

Dibromo-derivative.—Obtained by adding bromine to the alcoholic solution, it separated from absolute alcohol as a red microcrystalline powder, m.p. 175°. Alkaline solution does not fluoresce, while alcoholic solution fluoresces green. (Found: Br, 30·6. $C_{25}H_{16}O_3Br_2$ requires Br, 30·5 per cent.).

The dibenzoyl derivative crystallised from acetone ; it is insoluble in benzene, ether, alcohol, and chloroform. (Found: C, 81·5; H, 4·5. $C_{39}H_{26}O_5$ requires C, 81·5; H, 4·5 per cent.). Other products obtained by the condensation of resorcinol with open-chain monoketones are described in Table I.

Condensation with Cyclic Ketones.

Anhydride of Diphenyltetrahydroxydiphenylmethane.—Fluorenone (1·8 g.) and resorcinol (2·2 g.), were mixed with fused zinc chloride and heated in an atmosphere of hydrochloric acid gas for 3 hours. The product was washed with dilute hydrochloric acid, dissolved in sodium hydroxide solution, filtered and precipitated with dilute hydrochloric acid ; it was finally obtained from benzene as a bright yellow powder, m.p. 220° (yield, 85%). It is soluble in alcohol with a green fluorescence. It dyes wool and silk bright yellow. (Found: C, 82·1 ; H, 4·6. $C_{25}H_{16}O_3$ requires C, 82·4 ; H, 4·4 per cent.).

Chloroacetyl Derivative.—Obtained by boiling with chloroacetyl chloride for 15-20 minutes, it formed colourless microcrystals, m.p. 182° from a mixture of alcohol and chloroform ; it is easily soluble in chloroform but sparingly in alcohol. (Found: Cl, 13·5. $C_{29}H_{18}O_5Cl_2$ requires Cl, 13·7 per cent.). Other products of this series are described in Table II.

Condensation with Dkietones.

Condensation Product of Benzil and Resorcinol (*Formula* I, R= Ph, R′=Bz).—Benzil (4 g.) and resorcinol (4 g.) were heated as usual for 3—4 hours. The product was finally washed with benzene, ether, chloroform and crystallised from alcohol ; m.p. 215° (yield, 70%). It dyes wool red. (Found: C, 79·0 ; H, 4·7. $C_{26}H_{18}O_4$ requires C, 79·1 ; H, 4·5 per cent.).

Dipotassium Salt.—(Found: K, 16·8. $C_{26}H_{16}O_4K_2$ requires K, 16·6 per cent.). Other products of this series are described in Table III.

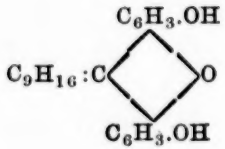
TABLE I.

Name.	Formula.	Method of preparation (R = resorcinol.).	M.p.	Analysis. Calc.	Found.	Properties.
Anhydride of heptahydroxytetraphenylmethane.	I, R = Ph, R′ = $C_6H_2(OH)_3$	R + trihydroxybenzophenone + fused $ZnCl_2$ + dry HCl gas at 180°–190° for 2–3 hours. Yield 80–85%.	No change up to 280°	C, 72·5 H, 4·3	72·8 4·4	Dark brown powder from alcohol. Insoluble in ether, benzene, chloroform, acetic acid. Caustic soda solution reddish-brown having green fluorescence.
Anhydride of tetrahydroxytriphenylmethylmethane.	I, R = CH_3, R′ = Ph	R + acetophenone + $ZnCl_2$ + HCl gas at 150°–160° for 2 hrs. and at 180–190° for 3 hrs. Yield 50–60%.	152°	C, 78·9 H, 5·2	79·1 5·3	Orange powder from alcohol. Sparingly soluble in benzene, ether, chloroform, acetic acid. Alkali solution orange and fluorescent (green). Dyes wool light orange.
,, Dibromo-derivative.	$C_{20}H_{14}O_3Br_2$		160°	Br, 34·6	34·8	Microcrystals from absolute alcohol. Insoluble in ether, chloroform, benzene, soluble in acetone.
,, Dibenzoyl derivative.	$C_{34}H_{24}O_5$		115°	C, 79·6 H, 4·6	79·7 4·5	Purified from acetone. Insoluble in ether, benzene, chloroform and alcohol.

TABLE I—*Contd.*

Name.	Formula.	Method of preparation (R = resorcinol).	M.p.	Analysis. Calc.	Found.	Properties.
Anhydride of tetrahydroxydiphenyldimethylmethane.	I, R, R′ = Me	R + acetone + $ZnCl_2$ + dry HCl gas, at 50° − 55° for 3 hrs. and at 180° − 190° for 4 hrs. Yield 30 − 40%.	165°	C, 74·3 H, 5·8	74·5 6·06	Orange red powder (alcohol). Insoluble in ether, benzene, chloroform, acetic acid. Soluble in acetone. Alkali solution light orange and fluorescent (green).
,, Dibromo-derivative.	$C_{15}H_{12}O_3Br_2$		153°	Br, 40	40·1	Purified from absolute alcohol.

TABLE II.

Condensation product of resorcinol and camphor.		R + camphor + $ZnCl_2$ + HCl gas at 180°-190° for 7—8 hours.	200°	C, 78·5 H, 7·1	78·2 6·7	Obtained from alcohol as a dark red powder. Insoluble in ether, benzene, chloroform, glacial acetic acid. Soluble in alcohol and acetone with green fluorescence. Dyes wool deep reddish-brown.
,, Dipotassium salt.	$C_{22}H_{22}O_3K_2$			K, 18·9	19·0	

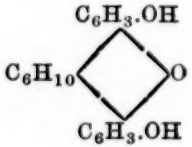
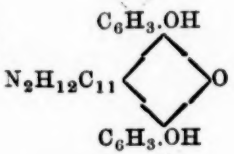
,, Dibenzoyl derivative.	$C_{36}H_{32}O_5$		120°	C, 79·4 H, 5·8	79·4 5·8	Microcrystalline red powder (alcohol) from acetone. Insoluble in alcohol, ether, benzene, chloroform.
,, Dibromo-derivative.	$C_{22}H_{22}O_3Br_2$		No change up to 280°.	Br, 32·3	32·4	Alkali solution deep red. Dyes wool bluish-red.
Anhydride of tetrahydroxydiphenyl*cyclo*hexane.		R + *cyclo*hexanone + $ZnCl_2$ + HCl gas at 150° for 3 hrs. and at 180°–190° for 3 hrs. Yield 74%.	Softens at 213° with decomposition.	C, 76·5 H, 6·4	76·3 6·5	Reddish-brown powder (rectified spirit). Soluble in alcohol and acetone. Insoluble in ether, benzene, chloroform, acetic acid. Alkali solution green fluorescent. Dyes wool and silk brownish-orange.
,, Dipotassium salt.	$C_{18}H_{16}O_3K_2$			K, 21·78	21·9	Violet powder.
,, Barium salt.	$C_{18}H_{16}O_3Ba$	Adding $BaCl_2$ solution to the potassium salt solution.		Ba, 32	33	Brownish-orange microcrystalline powder.

TABLE II—*Contd.*

Name.	Formula.	Method of preparation. (R = resorcinol).	M.p.	Analysis. Calc.	Found.	Properties.
,, Dibenzoyl-derivative.	$C_{32}H_{26}O_5$		Softens at 202°-203°	C, 78·36 H, 5·31	78·3 5·4	Microcrystalline powder from benzene. Soluble in acetone, chloroform, pyridine. Insoluble in alcohol, ether.
,, Dibromo-derivative.	$C_{18}H_{16}O_3Br_2$	By the action of Br in alcoholic solution.	No change up to 280°	Br, 36·36	36·4	Obtained from acetone as a red powder. Alkali solution red. Acetone solution red with green fluorescence. Insoluble in alcohol, ether, benzene, chloroform.
Condensation product of resorcinol and antipyrine.		R + antipyrine + $ZnCl_2$ + HCl gas at 180° − 190°, for 6 hrs. Yield 70%.	150°	N, 7·9	7·6	Obtained from alcohol as a dark brown powder. Alkali solution reddish-brown with green fluorescence. Insoluble in ether, benzene, chloroform. Dyes wool reddish-brown.
,, Dibromo-derivative.	$C_{23}H_{18}O_3N_2Br_2$		190°	Br, 30·1	30·2	Obtained from alcohol and acetone as a red powder. Dyes wool deep red.

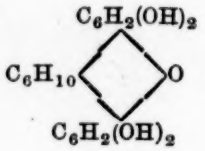
Anhydride of hexahydroxydiphenyl-*cyclo*hexane.		*cyclo*Hexanone + pyrogallol + $ZnCl_2$ + HCl gas at 180°–190°, for about 8 hrs. Yield 80%.	No change up to 280°	C, 68·79 H, 5·73	68·48 5·92	Black microcrystalline powder from alcohol; soluble in alcohol, acetone and pyridine; insoluble in benzene, ether, chloroform, petroleum ether. Dyes wool and silk a light yellow shade and iron-mordanted wool a brownish black shade.
,, Tetrapotassium salt.	$C_{18}H_{14}O_5K_4$			K, 33·47	33·5	Grey powder.
,, Dibarium salt.	$C_{18}H_{14}O_5Ba_2$	Adding $BaCl_2$ solution to the potassium salt solution.		Ba, 46·97	46·9	

TABLE III.

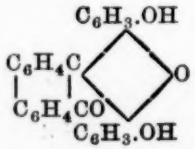
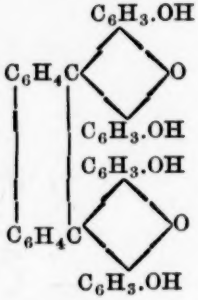
Condensation product of phenanthraquinone and Resorcinol (1 mol.).		Phenanthraquinone (1 mol.) + R (2 mols.) + $ZnCl_2$ + HCl gas at 170°–180°. Yield 80%.	160°	C, 79·58 H, 4·08	79·35 4·28	Soluble in alcohol and acetone with light blue fluorescence. Insoluble in ether, benzene, chloroform.

TABLE III—*Contd.*

Name.	Formula.	Method of preparation (R = resorcinol).	M.p.	Analysis. Calc.	Found.	Properties.
,, Dibenzoyl derivative.	$C_{40}H_{24}O$		148°	C, 80·0 H, 4·0	79·9 4·1	Soluble in toluene, insoluble, in alcohol, acetone, ether, chloroform, benzene.
Condensation product of phenanthraquinone (1 mol.) and resorcinol (4 mols.).		The above dihydroxy compound (1 mol.) + R (2 mols.) + $ZnCl_2$ + HCl gas at 190° −195° for 5-6 hrs. After alkali and acid treatment, washed with ether, benzene, alcohol and acetone. Yield 60-70%.	No change up to 290°	C, 79·1 H, 4·1	79·1 4·1	Crystallised from pyridine. Alkali solution reddish-brown with green fluorescence. Dyes wool reddish-brown.
,, Tetrabenzoyl derivative.	$C_{66}H_{40}O_{10}$		173°	C, 79·8 H, 4·0	79·8 4·1	Soluble in toluene.
,, Tetra-potassium salt.	$C_{38}H_{20}O_6K_4$			K, 21·4	21·5	

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